1997


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A STUDY OF THE EFFECT OF ENERGETIC FLUX BOMBARDMENT ON INTENSIFIED PLASMA-ASSISTED PROCESSING

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural Mechanical College
in partial fulfillment of the requirement for the degree Doctor of Philosophy

in
The Interdepartmental Program

in
Engineering Science

by
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December, 1997
ACKNOWLEDGMENTS

The author would like to extend sincere appreciation to Dr. Efstathios I. Meletis, his major Professor for the leadership and devotion to this work. His invaluable constructive guidance and encouragement were beyond measure. He would also like to thank Dr. Aravamudhan Raman for his encouragement and enthusiasm towards the research. His contributions are very much treasured. Sincere gratitude also goes to Dr. Evan Ma, Dr. John Collier and Dr. Don Kraft for their contributions in time and valuable suggestions in making the academic studies a success. To the technical staff in the machine shop he expresses his sincere gratitude, especially to Mr. Willie Dilworth who worked tirelessly to get projects underway.

He cannot pass without mentioning his wife, Beatrice Nana Ofosuah Adjaottor, whose tolerance, patience, support and encouragement have seen him through this journey.

He wishes to express to his parents his sincere thanks for building in him the strength to persevere in the face of all odds. To his uncle Sylvester Tetteh Adjaottor he is very grateful for his economic support that set him on the road to achieving this goal.

He also wishes to thank the Louisiana Educational and Quality Support Fund (Contract LEQSF 94-96-RD-B07) and RMI Titanium for their financial support during his studies.
# TABLE OF CONTENTS

ACKNOWLEDGMENTS ........................................................................................................... ii  
LIST OF NOMENCLATURE ................................................................................................ vi  
LIST OF TABLES ................................................................................................................ viii  
LIST OF FIGURES ............................................................................................................... viii  
ABSTRACT ........................................................................................................................... xiii  

CHAPTER  
I. INTRODUCTION ............................................................................................................ 1  
II. OBJECTIVES ................................................................................................................... 5  
III. REVIEW OF LITERATURE ........................................................................................... 6  
   A. Ion Beam and Plasma-Assisted Processes ................................................................. 7  
      1. Ion Implantation ..................................................................................................... 7  
      2. Ion Nitriding .......................................................................................................... 10  
      3. Physical Vapor Deposition .................................................................................. 15  
      4. Ion Beam Assisted Deposition ........................................................................... 16  
      5. Plasma-Assisted Chemical Vapor Deposition (PACVD) ........................................ 20  
   B. Intensified Plasma-Assisted Processing (IPAP) ......................................................... 23  
      1. Process Description and Characteristics ............................................................. 23  
      2. Theoretical Background ...................................................................................... 28  
      3. Mechanism of Plasma Nitriding ......................................................................... 34  
IV. EXPERIMENTAL PROCEDURES .................................................................................. 39  
   A. IPAP Processing System ......................................................................................... 39  
   B. Material .................................................................................................................... 48  
   C. Processing ................................................................................................................ 49  
   D. Characterization ....................................................................................................... 50  
      1. Surface Analysis .................................................................................................... 51  
      2. Transmission Electron Microscopy .................................................................... 51  
      3. Scanning Electron Microscopy .......................................................................... 52  
      4. X-ray Diffraction ................................................................................................. 52  

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5. **E. Property Assessment** ................................................................. 53
   1. Microhardness Measurements ........................................................ 53
   2. Wear Resistance ............................................................................ 54
   3. Fatigue Behavior ........................................................................... 54
   4. Corrosion Testing .......................................................................... 55

V. **RESULTS AND DISCUSSION** ............................................................. 56
   A. Effect of Glow Discharge Intensification on Plasma/Solid Interaction ........................................................................................................... 56
      1. Sputtering Studies ........................................................................ 56
         1.1. Sputtering in Intensified Plasma Processing ............................ 56
         1.2. Experimental Sputtering Yield Estimation ............................ 60
         1.3. Theoretical Predictions .......................................................... 62
         1.4. Discussion of Results ............................................................... 69
      2. Implantation Studies ..................................................................... 80
      3. Diffusion Studies ......................................................................... 92
         3.1 Characterization ..................................................................... 94
         3.2 Diffusion Analysis .................................................................. 100
         3.3 Discussion of Results ............................................................... 107
      4. Thin Film Deposition ................................................................... 111
         4.1 Film Characterization ............................................................... 111
         4.2 Discussion of Results ............................................................... 120
      5. Modeling ...................................................................................... 124
         5.1 Background of Model ............................................................... 124
         5.2 Model Description .................................................................. 133
         5.3 Model Verification .................................................................. 137
   B. Effect of Glow Discharge Intensification on Material Properties .... 142
      1. Microhardness Measurements ...................................................... 143
      2. Wear Resistance ........................................................................... 147
      3. Fatigue Behavior ........................................................................... 151
      4. Corrosion Testing ........................................................................... 153

VI. **CONCLUSIONS** ................................................................................. 156
   A. Sputtering Studies .......................................................................... 156
   B. Implantation Studies ....................................................................... 157
   C. Diffusion Studies ............................................................................ 157
   D. Deposition Studies ........................................................................... 157
   E. Model ............................................................................................. 158
   F. Properties of Modified Surfaces .................................................... 158

REFERENCES ............................................................................................... 160

iv

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LIST OF NOMENCLATURE

IPAP: Intensified Plasma-Assisted Processing
AES: Auger Electron Spectroscopy
XPS: X-ray Photoelectron Spectroscopy
TRIM: Transport of Ions in Matter
PMMA: Poly(Methylmetacrylate)
IBAD: Ion Beam Assisted Deposition
TEM: Transmission Electron Microscopy
SEM: Scanning Electron Microscopy
sccm: Standard cubic centimeter per minute
LIST OF TABLES

Table 1: Surface modification parameters used in the sputtering experiments. .................................................................58

Table 2: Fundamental plasma parameter values prevailing in sputtering experiments. .......................................................... 59

Table 3: Experimental results of sputtering yield. .............................................................63

Table 4: Sputtering yield estimation of Ar sputtering on Si by TRIM. ..............67

Table 5: Surface modification parameters for various treatments. ...............93

Table 6: Thickness of various layers and calculated effective diffusivities of nitrogen in Ti-6Al-4V. ............................................. 104

Table 7: Theoretical predictions of defect generation by Ar in Si. .............128

Table 8: Theoretical predictions of defect generation by Ar in TiN. ............ 128

Table 9: Theoretical predictions of defect generation by N in TiN. ............ 129

Table 10: Wear characteristics of PMMA on Ti-6Al-4V substrate in Ringer’s solution (5 N load and 0.1 m s⁻¹ sliding velocity). .... 150

Table 11: Corrosion properties of Ti-6Al-4V-base materials in deaerated Ringer’s solution at 36°C. ............................................. 154

Table 12: Estimated plasma parameters during IPAP and conventional ion nitriding of aluminum. .........................................181
LIST OF FIGURES

Figure 1  Typical depth distribution of nitrogen ions implanted into a material surface at various beam energies, keV, [3]. .........................8

Figure 2  Typical Ion Implantation unit [3]. ........................................................9

Figure 3  Glow discharge characteristic curve [3]. .................................................12

Figure 4  Schematic of energetic particle-surface interaction. .........................14

Figure 5  Thornton modification of the structure diagram for film growth illustrating the dependence of microstructure on the substrate temperature and sputtering gas pressure [35]. ........................................17

Figure 6  Schematic of an IBAD process using the dual ion beam configuration. One ion gun is used for sputtering atoms from a target and another ion gun is being used to bombard the growing film [48]. .................................................................19

Figure 7  Schematic representation of enhanced glow discharge system [67]. .................................................................24

Figure 8  Schematic of the abnormal glow discharge [67]. .................................27

Figure 9  The relationship between the average ion and neutral energies and L/\lambda [12]. ...............................................................33

Figure 10 The relationship between total ion and neutral energies and L/\lambda [12]. ...............................................................33

Figure 11 The energy distribution of neutrals and ions which suffer collisions [12]. .................................................................35

Figure 12 Schematic representation of enhanced glow discharge and film deposition system. ..................................................40

Figure 13 Schematic of modified IPAP chamber. ................................................41

Figure 14 Schematic of modified IPAP top plate. .................................................42

Figure 15 Detailed schematic of cathode assembly. .............................................45

Figure 16 Calibration chart of infrared gun. .........................................................47

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viii
Figure 17 A typical measured step of 8.8 μm created by Ar sputtering of TiN with $E_{\text{avg}} = 800$ eV .....................................................61

Figure 18 Sputtering yield change as a function of angle of incidence and particle energy. .................................................................66

Figure 19 Theoretical sputtering yield of Si by Ar on Si. ........................................68

Figure 20 Theoretical sputtering yield of Ti and N by Ar on TiN. .........................70

Figure 21 Theoretical sputtering yield of Ti and N by N on TiN (assuming no reaction). .................................................................71

Figure 22 Experimental and theoretical sputtering yield of Si by Ar on Si. ................72

Figure 23 Variation of sputtering yield with energy for Ar ions bombarding Cu (low energy) [112]. .....................................................73

Figure 24 Variation of sputtering yield with energy for Ar ions bombarding Cu (high energy). The various curves are results of Ar ions bombarding Cu presented by different authors [113]. ............74

Figure 25 Experimental and theoretical sputtering yield of TiN by Ar on TiN. ......................77

Figure 26 Experimental and theoretical sputtering yield of TiN by N on TiN. ................79

Figure 27 Representative Auger-electron-spectroscopic (AES) N-concentration profiles in 304-stainless steel [30]. .................................81

Figure 28 Plot of the enthalpy of formation of metal nitrides vs. the nitrogen (1s)/metal (2p3/2) XPS intensity ratio for the first-row transition metals [118]. .....................................................83

Figure 29 Theoretical predictions of Ar atom implantation into Si. ....................86

Figure 30 Theoretical predictions of Ar atom implantation into TiN. ....................87

Figure 31 Theoretical predictions of N atom implantation into TiN (assuming no reaction). .................................................................89
Figure 32 Representative Auger and XPS spectra from ion implanted specimens. .................................................................96

Figure 33 AES nitrogen concentration profiles for various Ti-6Al-4V alloy specimens implanted with nitrogen ions at three different energies and two dose levels. ...........................................97

Figure 34 Typical Auger spectrum of intensified plasma nitrided specimen. ....98

Figure 35 Bright field TEM micrograph showing characteristic TiN microstructure and corresponding diffraction pattern. .........................99

Figure 36 Bright field TEM micrograph showing significant distortion in TiN regions just below the outer surface layer. .......................101

Figure 37 Surface microhardness versus indentation load for various Ti-6Al-4V specimens implanted with nitrogen ions at three different energies and IPAP processed specimens. ..............102

Figure 38 Microhardness depth profiles for nitrogen ion implanted and IPAP processed Ti-6Al-4V specimens. .............................103

Figure 39 Ion energy distribution for the high ion energy (Ei a =1086 eV) IPAP nitriding treatment (L/λ =2.19). The solid line (L/λ =10) indicates the boundary between conventional and IPAP nitriding. .........................................................109

Figure 40 Variation of stoichiometry of TiNy films with substrate bias voltage. .................................................................112

Figure 41 Microhardness (Knoop at 25g) of TiNy films as a function of substrate bias voltage. .........................................................114

Figure 42 X-ray diffraction patterns of two TiNy films deposited at Vb = -80 V and Vb = -120 V. ..............................................116

Figure 43 Stoichiometry of TiCx films as a function of substrate bias voltage. The AES spectra were collected after 2 min of Ar+ sputtering at 2 keV. .................................................................118

Figure 44 Microhardness (Knoop at 25 g) of TiCx films deposited at various substrate bias voltage values. ..............................119

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Figure 45  Microhardness (Knoop) of TiC$_x$N$_y$ films as a function of N$_2$ flow rate and substrate bias. ..............................................................121

Figure 46 Interactions between incoming energetic atoms and substrate in the near-surface region. ...........................................................................125

Figure 47 Vacancy generation by N atoms in TiN. ..............................................130

Figure 48 Theoretical estimation of N vacancy generation and atom implantation depth in TiN. .................................................................132

Figure 49 Defect generation by energetic N particles (N$_2^+$ or N$_2$) in TiN during IPAP. .................................................................134

Figure 50 Auger profiles of intensified and low energy processed specimens [120]. .................................................................138

Figure 51 Logarithmic derivative of N concentration profile for intensified plasma processing. .................................................................139

Figure 52 Logarithmic derivative of N concentration profile for low energy process. .................................................................140

Figure 53 Surface microhardness measurements for Ti-6Al-4V specimens processed under intensified conditions for different processing times. .................................................................144

Figure 54 Observed surface hardness on both front and back of processed specimens. .................................................................145

Figure 55 Surface roughness variation of Ti-6Al-4V with power density changes. .................................................................146

Figure 56 Surface roughness changes of Ti-6Al-4V with processing time. ....148

Figure 57 Typical surface appearance of a Ti-6Al-4V alloy processed by IPAP for 2 hours (1 mA cm$^{-2}$, 2000 V), (a) overall appearance and (b) high magnification of (a). .................149

Figure 58 S-N curves for IPAP-processed smooth Ti-6Al-4V fatigue specimens. .................................................................152

Figure 59 Anodic polarization curves for TiN coating and Ti-6Al-4V substrate. .................................................................154
Figure 60  Auger spectra for specimens treated with IPAP and conventional ion nitriding showing the Al (LVV), N (KLL), O (KLL) and Al (KLL) transitions after 2 min sputtering. .........................170

Figure 61  SEM micrographs showing surface morphology of specimens produced by (a) high plasma energy IPAP and (b) conventional ion nitriding. In the right hand side of the micrograph the AlN film has been detached. .........................172

Figure 62  SEM micrograph showing an area close to the edge of a specimen nitrided by high plasma energy IPAP. .........................174

Figure 63  (a) Bright field TEM showing microstructure of Al3N synthesized by IPAP and (b) diffraction pattern from area shown in (a). .................................................................175

Figure 64  (a) Bright field TEM showing microstructure of AlN synthesized by plasma nitriding; (b) electron diffraction pattern of area shown in (a) and (c) dark field image by using a section of the (00.2) diffuse ring, which is the second ring shown in (b) corresponding to the AlN phase. The inner ring corresponds to the Mg2Si precipitates. ...............177

Figure 65  Surface microhardness measurements as a function of load for specimens nitrided with low and high energy plasma, IPAP. .................................................................178

Figure 66  Anodic polarization curves of IPAP treated (high energy plasma) and untreated 6061 Al alloy in 0.1 M NaCl solution. .................................................................180
ABSTRACT

An investigation of the plasma nitriding mechanism under intensified conditions (average particle energy up to 1200 eV) was carried out using a triode configuration. The significance of the different physical processes taking place during intensified plasma nitriding, such as sputtering, implantation, defect generation, redeposition and diffusion were investigated experimentally, while theoretical predictions were obtained by using the TRIM (transport of ions in matter) code. A titanium-base alloy was selected as the substrate material.

Sputtering yield in an inert atmosphere was found to exhibit three regimes as a function of incoming particle energy. The low energy and high energy regimes were found to be in agreement with the theoretical predictions while the intermediate regime showed a reduced level of sputtering yield independent of energy. This was the first time that such reduced sputtering yield was observed and was attributed to the onset of other physical processes such as generation of bulk defects (vacancies). Sputtering during nitriding was overshadowed by the development of the nitride layer.

Implantation studies showed that, N atoms can be implanted to the very near-surface region (<80 Å) and such effects can be realized at particle energies >200 eV. Theoretical predictions showed that vacancy generation initiates at particle energies >~300 eV and this process can exercise significant effects on N diffusion at energies >440 eV.

The present results suggest that the primary role in the intensified plasma process is played by the ions since they possess higher energies and their effect is complimented by the energetic neutrals. Enhanced diffusivities (five orders of
magnitude higher) were realized under intensified processing conditions over conventional processing.

In deposition experiments, a threshold energy was identified (~150 eV) that is required to produce grain refinement and the formation of a denser and stable nitride structure at the surface.

A model was developed on the premise that N diffusivity is proportional to the vacancy concentration and was consistent with the experimental evidence.

An assessment of important engineering properties showed that significant improvements can be achieved by intensified plasma nitriding.
CHAPTER I. INTRODUCTION

The majority of materials' functions may be related to surface behavior. Surface modification techniques can create unique new surface characteristics in materials and provide a promising solution to many engineering problems related to surface behavior (wear, friction, corrosion, oxidation, fracture initiation, etc.). This provides the opportunity to effectively utilize materials with 'tailored' surface properties, while keeping desirable bulk properties such as strength and rigidity [1]. Studies by the U.S. Department of Commerce show that surface technology is one of the key technologies that will dominate the 21st century. The need for new approaches in the conservation of engineering surfaces and the continuous quest for innovative methods to develop advanced materials make surface modification processes even more attractive.

During the last two decades, there have been tremendous developments in the field of surface modification methods. These technologies are gaining increasingly widespread industrial acceptance and have been the subject of several international conferences [2-6]. Most surface modification processes employ energetic beams and/or particles to alter the composition and/or structure at the surface and near surface region [7]. Different methods of surface modification lead to formation of three major kinds of modified surfaces. The first involves the deposition of a thin film or coating on the surface of interest. Processes for film or coating deposition include sputtering, ion plating, chemical vapor deposition (CVD), physical vapor deposition (PVD), and ion-beam-assisted deposition (IBAD). The second form of modification affects a thin layer
(less than 1 μm) under the original surface. Processes that accomplish this kind of surface modification include ion implantation and ion, electron, and laser beam annealing. These processes have a line-of-sight limitation. The third form of modification is achieved by plasma-assisted diffusion techniques such as plasma nitriding or carburizing. Plasma-assisted processes can produce a compound layer of controlled thickness under the original surface that can be followed by a diffusion zone. Processes in this category use the gas discharge phenomenon to produce energetic ions and neutrals under a vacuum environment, obtaining desirable three-dimensional coverage. Inert gas sputtering prior to processing generates energetic particles which effectively clean substrate surfaces. This feature significantly adds to the quality of the produced surfaces. The above capabilities make these processes very versatile and more economical as compared to ion beam techniques. At present, various plasma-assisted methods find an unusually broad field of applications ranging from diffusion barrier coatings in microelectronics to surface treatments of tool and machine parts [2-4,8,9]. Conventional plasma nitriding is conducted at high pressures (1-10 Torr), low voltages (300-1000 V) and relatively high temperatures which impose certain limitations such as processing of microstructure-sensitive materials. It has been established previously that the microstructure of modified surfaces is the key parameter in determining surface properties [1-6,10,11]. Processing parameters such as pressure and cathode current density are interdependent, hence limiting the capability, flexibility and control of conventional ion nitriding.
Recently, it has been demonstrated in our laboratory at Louisiana State University that plasma diffusion treatments at low pressures are feasible and can be performed effectively by using intensified glow discharge conditions (thermionically-assisted) in a triode plasma [12-15]. The technique, Intensified Plasma-Assisted Processing, IPAP [16], has the potential to combine plasma diffusion treatments with plasma-assisted vapor deposition and chemical-reaction synthesis. The novelty of the process is that it is conducted at low pressures and is characterized by a high degree of ionization thereby greatly improving the throwing power of the plasma, creating highly favorable surface conditions [12-15]. A major finding from the previous studies is that favorable surface conditions are created in IPAP, leading to the formation of desired nitrides and deep diffusion zones even in systems that are difficult or even impossible to nitride by conventional means. Furthermore, the growth rate of the compound layer and diffusion zone is significantly enhanced compared to conventional methods. Thus, significant improvements in properties ranging from thermal and chemical stability to wear resistance have been achieved [14]. Another important advantage is that processing can be conducted at low temperatures owing to low pressure.

Even though it is agreed that energetic flux favorably influences the compound formation and the development of a deep diffusion layer, the role of the energetic flux bombarding the substrate material is not well understood. Consequently, the motivation behind the present investigation was to study the fundamentals of the plasma/substrate interaction and their result in the modification process occurring during intermediate energy plasma-assisted processes such as IPAP. Advancing the knowledge in this new
area of surface modification will contribute not only to realizing the full potential of the IPAP process, but also of other plasma-assisted processes.
CHAPTER II  OBJECTIVES

Previous surface modification plasma and ion beam studies have concentrated on either extreme of the energy spectrum of participating particles. On the high energy end of the spectrum is ion bombardment by the process of ion implantation, 5-500 keV. Conventional ion nitriding, on the other hand, occupies the low energy end of the spectrum (ranging from thermal energy ~1-2 eV to ~200 eV). Current experimental evidence suggests that energetic particle bombardment at an intermediate range (200 - 1200 eV) [12-14], as present during IPAP, can have great beneficial effects in the surface modification process. A review of the literature shows that this issue has been completely unexplored.

This situation necessitates understanding the fundamentals which govern the relationship between glow discharge intensification and characteristics of the layers produced during ion nitriding. Thus, this research will focus on the effect of two governing fundamental glow discharge parameters, i.e., flux and energies of bombarding ions and neutrals. The overall objective is to develop a fundamental understanding of the role of the species involved in intensified plasma-assisted surface modification processing that will allow the design and development of new systems of interest, to fully exploit the potential of this technique in an unusually broad range of engineering applications.
CHAPTER III. REVIEW OF LITERATURE

Over the past one hundred years, materials have often been exposed to harsh conditions. Economic losses due to material degradation have been estimated at 8 to 10 percent of the Gross National Product. In a world of diminishing resources and heightened consciousness on economic viability, it is essential to find ways of reducing the materials degradation which increases cost. A number of novel processing methods are under investigation to meet various needs. However, several processes are used industrially without a good understanding of the fundamentals. It is evident that more research would expand and advance the novel techniques. The present work is a step in that direction. Surface modification processes offer a great opportunity to develop materials with unique surface properties without changing desirable bulk properties. These changes of the near-surface region of materials are extending from the nano level to several microns by forming ‘tailored’ thin films, stable and metastable compounds, and diffusion layers.

Based upon physical principles, the surface modification techniques can be classified as

(i) Energy or Ion Beam Techniques e.g. - Ion Implantation, Laser Processing, Ion Beam Mixing, etc.. These techniques use an independent ion or energy source with a line-of-sight limitation.

(ii) Glow Discharge Processes (GDP) e.g.- Ion Nitriding, Ion Carburizing, Ion Plating, etc.. These latter techniques use the gas discharge phenomenon.
(iii) Ion Beam Assisted Deposition. This process combines some aspects of both processes described above. A brief description of some representatives of these techniques is given below.

A. Ion Beam and Plasma-Assisted Processes

1. Ion Implantation

Ion implantation is mostly a non-thermal, non-equilibrium, physically driven ballistic alloying process producing a relatively shallow (<0.5 µm) modified layer [17-27]. Typical concentration profiles obtained by ion implantation are presented in Figure 1. The Gaussian distribution of nitrogen concentration in Figure 1 is developed by a collision cascade that is set up by the impinging energetic ions. The depth of penetration is controlled by the energy of the ions and their size in relation to the size of the atoms of the substrate material. A broad beam of ions of uniform energy is accelerated and directed onto the substrate that can be maintained at room temperature. Figure 2 shows a typical ion implantation unit. Typical energy of ions range from 5 to 500 keV. Ion implantation is carried out in high vacuum environments, 10<sup>-6</sup> Torr, in order to maintain a focused ion beam. Sputtering by the high energy beam limits the processing time and layer depth since a state of equilibrium is reached during processing (implantation rate equals sputtering rate). The case layer depth produced by ion implantation is determined by the collision processes that slow down the energetic ions as they strike and penetrate the implanted surface. In most materials, the range of
Figure 1  Typical depth distribution of nitrogen ions implanted into a material surface at various beam energies, keV, [3].
Figure 2  Typical Ion Implantation unit [3].

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penetration of the ions is less than 0.5 μm for accelerating potentials in the range of 100 keV. Higher implantation voltages do not produce dramatic increases in penetrated depth because of the nature of the stopping process.

Since ion implantation is a treatment method that only modifies surfaces in its line-of-sight, irregularly-shaped parts have to be manipulated in the beam throughout the treatment cycle. This manipulation can be cumbersome. Improvements in ion implantation to eliminate the line-of-sight limitation have been achieved through plasma source ion implantation [28] and plasma immersion ion implantation [29]. These new methods however, still have a depth limitation that can raise concerns for prolonged service life of treated components in certain applications. Nevertheless, the high impact of the ions during ion implantation makes it a favorable surface modification process for metastable, nonequilibrium and amorphous compounds formation. Property improvement in the areas of corrosion, fatigue crack initiation and wear have been reported by using ion implantation [18-23,30].

2. Ion Nitriding

The line-of-sight limitation as well as the shallow modified layer of ion implantation is overcome in ion nitriding where a glow discharge fully engulfs the substrate to ensure complete uniform surface treatment and creation of deeper layers. Ion nitriding is a plasma technique involving mainly thermal diffusion treatment of nitrogen into the substrate material. This treatment along with carburizing has been mainly applied in the past to increase surface hardness and improve fatigue and wear
performance of various steel components such as crankshafts, gears, bearings, dies and cutting tools [31].

Conventional ion nitriding is a diode process conducted at relatively high pressures, 1 to 10 Torr, and low bias voltages, 300-1000 V. The workpiece is made the cathode with a negative bias while the chamber is maintained at ground potential. When a high enough voltage is applied to the cathode in the presence of a gas operating under vacuum, a glow discharge is produced, when molecules of the gas are ionized by colliding with electrons generated from the workpiece. The ionization of the gas sustains an electrical current which involves a flow of electrons from the workpiece to the anode. This current simultaneously maintains a positive-ion flow from the gas mixture to the workpiece being treated. The pressure of the system controls the current density of the plasma. The diode system is usually operated in the abnormal glow discharge where the highest increase in current density as a function of bias voltage is observed (Figure 3). In order to sustain the plasma, diode systems are operated at high pressures which result in high surface temperatures. The high pressure leads to a plasma with a low average energy of particles (ions and neutrals). Approximately less than 0.005% of the ions in such plasmas have the maximum energy [32]. The low average energy of the plasma is made up of a large number of low energy (thermal) neutrals and a very small number of energetic ions and neutrals. The energetic particles activate the nitrogen molecules to speed up the reaction process. The main advantages of plasma nitriding compared to traditional nitriding processes which are carried out by using high temperature gaseous media or liquid baths (around 1000°C), are relatively
Figure 3  Glow discharge characteristic curve [3].
lower processing temperature, reduced processing time, energy savings and reduced environmental pollution.

Sputtering of adsorbed species from substrate surfaces is an established surface cleaning step during plasma processing. Figure 4 shows a schematic of the interaction between energetic particles and the substrate surface. Even though the concept of collision cascades is accepted as a part of sputtering, the basic processes responsible for sputtering differ among researchers. The views presented for the process of sputtering are that (i) the majority of atoms are sputtered by random collision processes, even in crystals [83-86], and (ii) regular lattice structure causes other random collision processes to dominate sputtering of both single and polycrystals [87,88]. There are also two views on the source of sputtered particles. Some researchers [83,84,86] are of the view that mostly surface atoms account for sputtering yield, whereas others like Brandt [85] argue that a great deal of sputtered atoms must have traveled some distance through the crystal before being ejected.

A qualitative picture of the sputtering of a random target by an energetic particle such as an ion is thought to follow the following steps:

(i) An impinging particle undergoes a series of collisions in the target, and atoms that recoil with sufficient energy undergo secondary collisions, thereby creating another generation of recoiling atoms.

(ii) Both the particle itself and energetic recoil atoms have the possibility of getting scattered back through the surface by a series of collisions from a depth in the immediate surface region. These account for a minor portion of the number of sputtered atoms.
Figure 4  Schematic of energetic particle-surface interaction.
(iii) Atoms originally located within a couple of atomic layers from the surface with small energies and range of travel are easily sputtered off hence constituting a major portion of the sputtering yield.

Diode ion nitriding consists of an improvement over the traditional process, but still extended periods of time are required for the development of deep diffusion zones, and nitriding is feasible only for certain materials (i.e., mainly steels). Moreover, the thermal neutrals raise the surface temperature, therefore restricting the processing of heat-sensitive microstructures. Most of these disadvantages can be overcome by IPAP which is described in a later section.

3. Physical Vapor Deposition

Ion implantation and ion nitriding produce layers that grow into the substrate surface, while physical vapor deposition grows a discrete layer on the substrate surface. Physical vapor deposition processes involve the transfer of mainly neutral species of a metal onto a substrate. Contamination on the surface easily reduces the adherence of the film leading to poor surface modification. Physical vapor deposition processes include thermal and electron beam evaporation, molecular beam epitaxy and sputtering. Improvement in film adherence can be achieved by applying in-situ cleaning processes such as in Plasma-Assisted Vapor Deposition. The ionic bombardment, sputtering from the plasma maintains a clean surface, creates surface defects which act as nucleation sites for film growth, promotes film adhesion, and increases film density [33,34].

Ion plating is a generic term applied to atomistic film deposition processes in which the substrate surface is subjected to a flux of energetic ions sufficient to cause
appreciable sputtering before and during film formation. Principal benefits from the ions during the ion plating processes are their ability to:

(i) sputter-clean the surface and maintain it clean until the film begins to form;

(ii) alter the surface and interfacial structure by sputtering and introducing high defect concentration, thus physically mixing the film and substrate materials, creating graded interfaces and

(iii) increase surface temperatures, thus enhancing diffusion and adatom mobility at the surface region producing a Zone III grain structure (Figure 5).

The above-stated benefits result in adherent films with dense and more randomly oriented microstructures [36]. Modern ion plating systems often use some form of plasma intensification such as thermionic emission, arcing, radio frequency (RF) or magnetic fields, e.g., magnetron sputtering [34,37-39], to increase the ‘throwing power’ of the particles impacting the substrate surface. The increased energy of the ions makes possible the growth of dense and adherent films with an equiaxed grain structure [36]. Some sources of vapor for ion plating are (i) metal-bearing gas, (ii) arc, (iii) sputtering, (iv) resistance heating, (v) focused electron beam, and (vi) plasma evaporation. Reactive gas ion plating can form ceramic films such as TiN, CrN, etc., by introducing a reactive gas like nitrogen in the presence of the evaporant metal particles [40,41].

4. Ion Beam Assisted Deposition (IBAD)

With IBAD, the beneficial effect of the bombarding particles in ion plating has been extended by supplying an additional external source of energetic particles to
Figure 5  Thornton modification of the structure diagram for film growth illustrating the dependence of microstructure on the substrate temperature and sputtering gas pressure [35].
bombard the depositing film. The deposition of a film in the presence of an ionized atmosphere provided by an external source constitutes Ion Beam Assisted Deposition. It is a modification of the conventional PVD process in which the growing film is bombarded with an energetic ion beam. Four typical configurations used for IBAD processes are:

(i) low energy Kaufman source used with an electron beam evaporator;
(ii) high energy ion beam from an implanter used with an electron beam evaporator;
(iii) dual ion gun system (where a Kaufmann source produces an atomic flux by sputtering a target and the other Kaufmann gun is directed at the substrate surface); and
(iv) an ionized evaporant stream alone or with molecular beam epitaxy (MBE) sources.

Figure 6 shows a representative schematic of an IBAD process using the dual ion beam configuration. One ion gun is being used to sputter atoms from a target and another ion gun is being used to bombard the growing film on the substrate holder.

IBAD causes various changes on films being deposited on substrates. Among the changes effected on films are film densification [42,43], increased oxidation resistance in optical films [44], minimization or elimination of columnar microstructure, alteration of the state of stress from tensile to compressive stress, alteration of the average grain size and the preferred grain orientation [42,45], increased film/substrate adhesion [33], enhanced conformal coverage, 'low-temperature' epitaxy [46], enhanced
Figure 6  Schematic of an IBAD process using the dual ion beam configuration. One ion gun is used for sputtering atoms from a target and another ion gun is being used to bombard the growing film [48].
surface chemical reactions, tailoring film composition, lowered metal resistivity and growth of metastable phases [47,48].

Some beneficial effects of ionic bombardment are discussed below. Ionic bombardment during processing leads to the production of defects in the substrate surface which act as preferred adsorption sites. These sites trap incident species in the near-surface region. Grain size may be increased or decreased by energetic particle bombardment. If nucleation sites continue to be formed on existing grains, the final result is a high density of small, randomly oriented grains. This leads to a decrease in film porosity. If energetic particle bombardment primarily deposits energy in the near-surface region without leaving permanent defects, then it tends to increase surface mobility and subsequently increase the grain size. Thermodynamically metastable phases have been grown using IBAD, e.g., diamond-like carbon and semiconductors of the form (III-V)_{(1-x)(IV)_x} such as (GaAs)_{(1-x)}(Ge)_x [47]. The primary role of ion irradiation in the growth of diamond-like carbon, for example, appears to be the preferential removal of sp\(^2\) trigonal graphitic C bonds in favor of sp\(^3\) tetrahedral diamond bonds [49].

5. Plasma-Assisted Chemical Vapor Deposition (PACVD)

IBAD basically grows films by depositing material not very different than the source target, but chemical vapor deposition involves completely different reagents chemically combining to form a third product which is deposited on the substrate as a film. Chemical vapor deposition of coating is a broad field finding applications in microelectronics, tribology, corrosion, etc. [50-55]. One prominent application of
PACVD has been in the deposition of diamond-like carbon films [52,53]. Conventional CVD requires very high substrate temperatures in excess of 800°C to ensure the necessary reactions for surface modification. Such high temperatures are detrimental to microelectronics substrates such as aluminum (which will melt) or polymers (which will decompose) as well as metals or alloys that undergo phase transformation, for example austenitic stainless steels. PACVD offers a method of surface modification that can be carried out at lower temperatures.

In CVD, the depositing species are created from precursor gases which, without energy input, are not in themselves condensable. In the conventional CVD process, the substrates are heated to high temperatures to cause the precursor gases to decompose. However, in a plasma deposition process, the ions and neutrals receive energy in the plasma producing a wide variety of species of the molecular precursor gas. The plasma can be of two types: thermal plasma, as created in an arc discharge at atmospheric pressure and cold plasma, as created in a low pressure glow discharge. The electrons, ions, and neutral gas molecules in a thermal plasma are in thermodynamic equilibrium. However, in the cold nonequilibrium plasma, the electrons, and to a smaller extent, ions, are considerably more energetic than the neutral gas molecules. The species of the molecular precursor gas are created by the electron impact dissociation, excitation and ionization of the gas molecules. The primary function of the plasma is to generate chemically active ions and free radicals which overcome the activation barrier to the chemical reaction and therefore react with other ions, atoms, and molecules in the gas phase or at the substrate surface to induce chemical reactions at low temperatures. The
number density of condensable neutrals is much higher than that of ions. Film growth is therefore dominated by bonding of neutral radicals. Three main plasma generating sources exist: direct current (DC), RF and microwave (MW). DC plasmas generate radicals close to the substrate surface resulting in heterogeneous reactions and higher deposition rates than in RF and MW source reactors. RF and MW plasmas generate radicals in the bulk of the plasma making it more prone to the occurrence of gas-phase reactions (homogeneous reactions) [56]. The plasma deposition process can be conceptualized as being two subsequent processes. The first involves the formation of condensable species which are mostly electrically neutral. The second is the mass transport by convective diffusion of these radicals to the surface of the growing film. Ion bombardment may not contribute much to film growth but can adversely affect the properties of the deposited film if the ion energy is large (more than 20 eV) [54].

A variation of the PACVD is called the plasma afterglow CVD. It is basically a variation of the design in reactor where the reactive constituent is introduced in the afterglow zone of the reactor, e.g., electron cyclotron resonance (ECR) reactor [57,58], remote RF/MW plasma CVD reactor [52,59]. The distinction between the afterglow process and the conventional plasma processes is that in the afterglow technique only certain desirable 'active' species formed in the discharge are introduced into the reaction zone. By contrast, in the conventional plasma processes all different kinds of species are generated and react with the substrate. These are measures to improve the capabilities of PACVD.

PACVD has been very beneficial to the microelectronics industry. However, even in semiconductor wafer fabrication, the conventional PACVD process can cause
undesirable plasma-substrate interaction such as incorporation of undesirable species in the film or damage due to plasma bombardment. This problem is being tackled by the use of the afterglow reactor. Undesirable compressive stresses generated in the deposit particularly at the lower frequencies renders the films conducive to spalling and cracking. Also, PACVD films often form columnar structures because of the incomplete coalescence of growing islands on the substrate surface. These films cannot withstand harsh corrosive and wear environments because of the porosity and weakness of the improperly adhered columnar structure [60].

B. Intensified Plasma-Assisted Processing

The preceding descriptions were about existing processes which operate either with high energy particles (5 - 500 keV) as in ion implantation or low energy particles (ranging from thermal energy ~1-2 eV to ~200 eV) as in ion nitriding. A process description and characteristics of IPAP which operates in a range involving energetic particles with an intermediate energy level (about 200 - 1200 eV) follows next.

1. Process Description and Characteristics

Intensified Plasma-Assisted Processing is a technique recently developed [12-16]. IPAP employs a glow discharge in a triode configuration as shown in Figure 7 allowing processing at low pressures and control of current density independently of other process parameters such as bias voltage and pressure. This permits processing at relatively low temperatures coupled with highly energetic flux compared to the conventional plasma nitriding. The relatively low temperature of operation affords not
Figure 7  Schematic representation of enhanced glow discharge system [67].
only the processing of microstructure-sensitive materials, but also control of the energetic flux to synthesize desirable nitrides and generate beneficial surface effects such as vacancies and dislocations that can serve as compound nucleation sites.

Glow discharge intensification can be achieved in several ways including the use of an electron emitter, RF fields and magnetic fields. Using a thermionic emission system is one of the most effective ways [13,62]. In this case thermionically emitted electrons are attracted by a positive electrode, gain energy and in their path collide with and ionize gas molecules in the plasma. Also the positive electrode which applies a small voltage (70-110 V) avoids electron accumulation in the vicinity of the filament. The supply of extra electrons offers flexibility to the control of the glow discharge. Process parameters such as the cathode current density, cathode voltage and chamber pressure can be independently controlled providing the following advantages over the conventional glow discharge [32,37,62]:

(i) high plasma density or a high ionization efficiency;
(ii) sustained plasma at a lower pressure and low cathode voltage;
(iii) an increase in the energy of the particles;
(iv) greater control over the glow discharge and energetic particle bombardment;
(v) reduced substrate temperature.

In the past, the intensification of the plasma has enabled the surface processing of difficult materials like austenitic stainless steel [13], pure Ti, and Ti alloys [14] and aluminum [15]. Conventional ion nitriding of stainless steel requires dilution of the plasma with hydrogen in order to form the desirable high nitrides of iron and eliminate the formation of low nitrides such as brittle Fe$_4$N called ‘white layer’. IPAP

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successfully nitrided AISI 304 stainless steel at relatively low temperatures producing high nitrides, composed of a thin FeN layer followed by a thick layer of Fe$_2$N and Fe$_3$N [13]. IPAP of aluminum produced dense aluminum nitride with ultra-fine microstructure with a grain size $< 80 \, \text{Å}$ [15]. Treatment of pure Ti and Ti-6Al-4V alloy resulted in the formation of desirable surface compounds (TiN and Ti$_2$N) and long nitrogen diffusion zones [14]. Nitriding of Ti alloys by the conventional process has been extremely difficult in the past and processing has to be conducted above the $\alpha/\beta$ transformation temperature (~880°C) producing undesirable effects (differential expansion, residual stresses, microstructural changes, etc.). Furthermore, nitrogen effective diffusivities have been found to increase significantly (2-3 orders of magnitude depending on the system) during IPAP compared to the low energy process [13,14]. These achievements are attributed to the higher energetic bombardment prevailing in IPAP, but a clear understanding of these effects has not been developed yet.

The glow discharge in IPAP operates in the abnormal regime as shown earlier in Figure 3. The space between the cathode and the anode is divided into three regions: (i) the ion sheath near the anode, (ii) the cathode dark space and, (iii) the negative glow between the anode and the cathode. These three zones are schematically shown in Figure 8. The area of greatest interest to ion nitriding is the cathode dark space. It is in this region that the ions obtain their energy since this is the region of greatest potential drop. The mathematical characterization of glow discharges by plasma physicists has been an area of interest to help understand glow discharge generation and control.
Figure 8  Schematic of the abnormal glow discharge [67].

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2. Theoretical Background

Previous work at LSU [12] as well as by other researchers [5-7] has demonstrated that the main theories and equations developed by early plasma physicists to determine the dark space length and the ion energy distributions for the conventional glow discharge are applicable to enhanced glow discharge. The dark space length, \( L \), can be determined by the free fall Child-Langmuir equation [63]:

\[
L = \left( \frac{4 \varepsilon_0}{9 J} \right)^{1/2} \left( \frac{2q}{M} \right)^{1/4} V^{3/4}
\]  

(1)

where \( \varepsilon_0 \) is the permittivity of free space (8.85x10^{-12} F m^{-1}), \( J \) is the cathode current density, \( q \) is the ionic charge (1.6 \times 10^{-19} C), \( M \) is the ion mass (\( M = 4.66 \times 10^{-26} \) kg for \( N_2^+ \)), and \( V \) is the bias cathode voltage (\( V = V_c - V_p \), \( V_p \) being 10 V above the anode voltage). In the intensified plasma, \( N_2^+ \) is considered to be the primary ionic state as confirmed by measurements in triode systems [39,62,64]. The mean free path for charge exchange collisions, \( \lambda \), is expressed as:

\[
\lambda = \frac{1}{\eta \sigma}
\]  

(2)

where \( \eta \) is the gas density and \( \sigma \) the collision cross-section (2.5x10^{-15} cm^2 for \( N_2^+ \)) [64].
For the incident ion energy range of interest, 200-1200 eV, the change in $\sigma$ is negligible [32,62,65].

Some of the ions entering the dark space undergo collisions with neutral molecules resulting in energy loss by the ions before reaching the cathode surface. The ions transfer their energy to these neutrals. This symmetrical transfer collision mechanism

$$N_{2\text{FAST}}^+ + N_{2\text{SLOW}} \rightarrow N_{2\text{SLOW}}^+ + N_{2\text{FAST}}$$

is established to be the dominant process in the cathode dark space [64]. Other ions, however, escape collision and arrive at the cathode with their full energy. As a result the ions and activated neutrals have a distribution of energy. The energy distribution of ions and neutrals within the dark space has been described by Davis and Vanderslice [66] and by Rickards [67] who modified the Davis and Vanderslice model. For the ions arriving at the cathode, the energy distribution can be described by [66]:

$$\frac{dN}{dE} = \frac{N_i}{2} \frac{L}{\lambda} (1 - E)^{1/2} \exp\left[ -\frac{L}{\lambda} + \frac{L}{\lambda} (1 - E)^{1/2} \right]$$

(3)

where $N_i$ is the number of ions entering the dark space, $E$ is the ion energy (normalized to the cathode voltage, $V_c$). Assumptions made in deriving this equation are that:
(i) all ions originate in the negative glow;

(ii) in a charge exchange collision, an energetic ion interacts with its neutral counterpart, producing an equally energetic neutral and an ion with zero energy;

(iii) the collision cross-section for charge transfer is independent of incident ion energy; and

(iv) the electric field decreases linearly from the cathode to the edge of the negative glow.

Rickards modified the expression into a general form to accommodate electric field distributions other than the linear case assumed earlier [67]. The modified expression for ion energy distribution is given as:

$$\frac{dN}{dE} = \frac{N_i}{m} \frac{L}{\lambda} \left(1 - E\right)^{(1/m) - 1} \exp\left[-\frac{L}{\lambda} + \frac{L}{\lambda} \left(1 - E\right)^{1/m}\right]$$ (4)

When $m = 2$, the equation is equivalent to the Davis and Vanderslice model. When $m = 4/3$, the field corresponds to space charge limited (free-fall) case. It has been shown that the value of $m$ chosen has little effect on the distribution shape [62].

From the above expression, it can be shown that the energy of ions that suffered collisions is:
\[ E'_i = \int E N(E) dE = N_i V_c \left[ 2\left(\frac{\lambda}{L}\right)^2 - 2\left(\frac{\lambda}{L}\right)^2 e^{-\frac{L}{\lambda}} + 2\left(\frac{\lambda}{L}\right)^2 e^{-\frac{L}{\lambda}} \right] \] (5)

The number of ions escaping any collisions with neutrals and therefore arriving at the cathode with their maximum energy is:

\[ N_f = N_i e^{-\frac{L}{\lambda}} \] (6)

The total energy of these highly energetic ions is given as:

\[ E'' = V_c N_i e^{-\frac{L}{\lambda}} \] (7)

Thus the total ion energy \( E'_i \) is:

\[ E'_i = E'_i + E'' = N_i V_c \left[ 2\left(\frac{\lambda}{L}\right)^2 - 2\left(\frac{\lambda}{L}\right)^2 + 2\left(\frac{\lambda}{L}\right)^2 e^{-\frac{L}{\lambda}} \right] \] (8)

Since the plasma is composed of ions and neutrals with a range of energies, an approximate estimate of the average ion energy, \( E'_i^a \) is given by [61]:

\[ E'_i^a = V_c \left[ 2\left(\frac{\lambda}{L}\right)^2 - 2\left(\frac{\lambda}{L}\right)^2 + 2\left(\frac{\lambda}{L}\right)^2 e^{-L/\lambda} \right] \] (9)
The energy distribution function for the neutrals is rather difficult. However, it is noticed that the energy lost by the ions during collision is gained by the neutrals. This means therefore that the number of neutrals is equal to the number of collisions in the dark space which can be expressed as

\[ N_n = N_i \frac{L}{\lambda} \quad (10) \]

Thus the average energy of the energetic neutrals is also given as [61]:

\[ E_n^* = \frac{E_n^i}{N_i} \frac{L}{\frac{L}{\lambda}} = V_e \lambda \frac{\lambda}{L} \left[ 1 - 2 \left( \frac{\lambda}{L} \right) + 2 \left( \frac{\lambda}{L} \right)^2 - 2 \left( \frac{\lambda}{L} \right)^2 e^{-\frac{\lambda}{L}} \right] \quad (11) \]

It is evident from the above equations that the ratio \( L/\lambda \) greatly influences the average energies of the ion and neutrals. Figure 9 shows that the average energies of the ions and the neutrals increase with decreasing \( L/\lambda \) values. The low \( L/\lambda \) ratios are achieved under conditions of low pressure and glow discharge intensification. Under such conditions, the mean free path for charge exchange collision, \( \lambda \), increases, thereby creating a cathode dark space with virtually no collisions. The ions therefore arrive at the cathode with most of their energy gained in this region. Since the neutrals gain their energy from the ions, they are of lower energy levels. The total energy of ions decreases, while the total energy of the neutrals increases with increasing \( L/\lambda \) ratio as shown in Figure 10.

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Figure 9  The relationship between the average ion and neutral energies and $L/\lambda$ [12].

Figure 10  The relationship between total ion and neutral energies and $L/\lambda$ [12].

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This trend occurs because increased $L/\lambda$ ratio corresponds to increased pressure with decreased mean free path for charge exchange collision, $\lambda$. This results in increased collisions of the gas molecules thereby creating a large number of neutrals and fewer energetic ions. Earlier work in this laboratory has shown that a critical $L/\lambda$ ratio of about 2 optimizes the effect of the energetic particle bombardment as shown in Figure 11 [12]. This can be attributed to the effectiveness of energy distribution. It was postulated that at $L/\lambda = 2$, an optimum distribution of energy among ions and neutrals is obtained. While it is recognized that beneficial effects must derive from an 'efficient' particle bombardment, at the moment it is not at all clear why the bombardment by the energetic flux (300-1000 eV) in the IPAP process can have such long lasting effects deep under the material surface. Additional work is needed to develop a better understanding of the relation between energy distribution of ions and neutrals and their effect on the modification process in the near surface region of the material.

3. Mechanism of Plasma Nitriding

Plasma nitriding has been well established as an industrial process, though, however, its mechanism is still not well understood. In the past, several studies have been conducted to elucidate the plasma nitriding mechanism, but little agreement has been reached up to date. The main issue of contention concerns the nature of the active particles involved in the plasma during the nitriding process. Several researchers have attributed nitriding to neutral nitrogen atoms. Seybolt [68] proposed that nitride formation during ion nitriding is simply a thermal diffusion process. It was suggested
Figure 11 The energy distribution of neutrals and ions which suffer collisions [12].
that the absorption of neutral nitrogen atoms on the surface of a substrate and the
subsequent diffusion into the subsurface are the reasons for nitride formation. Tibbetts
[69] performed experiments using a d.c. plasma where the workpiece was nitrided with
and without a grid that repelled cations. It was reported that neutral atomic nitrogen
was capable of causing effective nitriding. By using several analytical techniques,
Taylor et al. [70] and Hangstrum [71] examined the in-situ nitrogen interaction with
silicon and its oxides. They deduced that the N$_2^+$ ions undergo charge exchange and
dissociation at the surface of the substrate to form neutral nitrogen atoms, which then
react to form nitrides. More recently, it was also suggested [72-74] that the formation
of the nitrided layer occurs by the penetration of active nitrogen atoms produced by
collision dissociation. During this process, high energy ions collide with nitrogen
molecules which dissociate producing active N atoms that subsequently form the
nitride. Similarly, Matsumoto et al [75] in their study concluded that the rate-
determining step for Ti, Zr, Si and steel plasma nitriding is the surface adsorption of N
and NH radicals.

An opposite view proposed by other researchers was that ionic species were
responsible for plasma nitriding. As early as 1957, Shockley [76], suggested that the
thin irradiated surface layer can act as a source for vacancies and interstitials. The
notion of gas absorption and diffusion carried over from gas nitriding led Hudis [77] to
study the mechanism of ion nitriding of steels. It was reported that gas absorption is not
a dominant ion nitriding mechanism. The surface hardness, which relates to the
nitrogen content, was found to increase with increasing current density. Hudis
therefore, attributed the plasma nitriding reaction of steels, to ionic bombardment of the cathode. It was suggested that the species responsible for the nitriding process are NH$_x$ ions. Jones and Martin [78] also developed a model arguing that ion bombardment promotes diffusion of nitrogen by the creation of surface defects. Kölbel [79] and Edenhofer [80,81] argue that the ions are the main active particles in the ion nitriding process and consider that the ion sputtering process plays a major role. Lakhtin and Krymskii [82] claimed that surface cleaning and increased surface activation by the ionic bombardment are the main reasons for the nitride layer formation at the surface. Further evidence on the role of ionic species was presented by Brokman and Tuler [9] who applied a magnetic field in order to sustain the gas discharge at lower pressures. They magnetically directed only the ions onto the substrate surface, showing that the local effective nitrogen diffusivity is proportional to the cathode current density. This revelation led them to propose that ion bombardment promotes the diffusion of nitrogen by creating defects such as vacancies, and forming vacancy-ion pairs. The vacancy-ion pairs then diffuse substitutionally having a much higher diffusivity compared to interstitial nitrogen diffusion.

In spite of the controversy regarding the mechanism, a careful examination of the above models shows that the energetic particle bombardment is of primary importance to all cases. In conventional ion nitriding, the average particle energy is low since the process is dominated by a large number of low energy neutrals. In the enhanced glow discharge process a large variation of ion and neutral energies can be obtained allowing the study of their effect on the modification process. Furthermore, conventional plasma nitriding is limited mainly to nitriding of steels, while the
enhanced process allows nitriding of new systems, thus providing the opportunity to clarify further the mechanism, since new microstructures are involved.
CHAPTER IV. EXPERIMENTAL PROCEDURES

A. IPAP Processing System

A new surface modification system was designed and constructed during the course of the present work. The system allows three modes of operation to be conducted, namely plasma treatments, ion beam treatments and sputter deposition. A schematic representation of the system is shown in Figure 12. The unit consists of a base plate connected to the mechanical and diffusion pumps, a cylindrical stainless steel chamber and a top plate supporting the specimen holder. All three system components have ports to accommodate electrical and mechanical feedthroughs. The base plate is 50 cm in diameter and carries eight 2.54 cm ports. The stainless steel chamber is 46 cm in internal diameter, 56 cm in height and carries twelve conflat flanges of various sizes as shown in Figure 13. Finally, the top plate has a thickness of 2.54 cm and carries a central 10 cm diameter port used for the cathode (specimen holder) assembly along with five peripheral 2.54 cm ports (Figure 14). The locations of the top plate ports and chamber flanges were designed in such a way as to accommodate all current processing requirements and provide some versatility for future additions to the system.

A 3 cm filamentless broad beam ion source by Anatech Ltd. is attached to the bottom plate and is connected to electrical and gas feedthroughs utilizing two of the bottom plate ports. The ion source is powered by Anatech's model IS-3000 power supply capable of delivering energetic particles in the energy range of 5 eV to 1200 eV. The ion gun is mounted on a swivel collar mount allowing height, tilt and rotational motion. The ion source is angled towards the specimen surface for a uniform ion beam...
Figure 12  Schematic representation of enhanced glow discharge and film deposition system.
Figure 13  Schematic of modified IPAP chamber.
Figure 14  Schematic of modified IPAP top plate.
bombardment, Figure 12. The ion beam source can be utilized for plasma enhancement or for ion beam deposition by feeding the appropriate gas (e.g., Ar, N₂, CH₄, etc.).

A Torus 2 d.c. magnetron sputtering source with a 5 cm diameter target is also attached to the bottom plate. It is powered by the MDX 500 magnetron drive (Advanced Energy) and has a sputtering power of 1 kW. A vacuum interlock is connected to the power supply and acts as a safety measure by turning off the power when pressure in the chamber reaches 1 Torr. The magnetron unit has a 21 cm long stem, carrying power, water cooling and allowing height adjustment of the source. The magnetron is flex-mounted to permit ±30° tilting in the vertical axis, which allows axial positioning of the target towards the specimen surface, Figure 12. Deposition is achieved by introducing an inert gas (i.e. Ar) into the chamber to sustain a plasma and sputter the desired target material that deposits onto the substrate. Reactive sputter deposition can be achieved by introducing the appropriate gas into the chamber to react with the sputtered species and deposit onto the substrate. The growth rate and thickness of depositing thin films are monitored by a Leybold Inficon IPN-750-211-G1 thin film sensor. The sensor is installed close to the specimen inline-view from the magnetron and ion beam source and regulated by an LH Inficon deposition monitor (model XTM/2) which displays the deposition rate, thickness and elapsed time.

The plasma intensification system is composed of a thermionic emission filament and a positive electrode. A 0.05 cm diameter thin tungsten wire is used as the thermionic filament (supplied by R.D. Mathis company). The wire is 5 cm long with six coils, and is horizontally suspended in the chamber by a pair of 0.6 cm diameter
copper rods that are connected to a two-pin high current feedthrough. The filament is powered by a low voltage/high current transformer capable of delivering a 2 kW power. A stainless steel plate (8 cm x 6 cm) is used as the positive electrode and is positioned diametrically opposite from the filament. The positive plate is operated by a 250 W low current HCR power supply (model 150-2-110). Voltage is applied to the plate through an electrical feedthrough (15 A rating) attached to a 3 cm conflat flange. The filament and positive plate are positioned at a height of about 46 cm from the base plate and lay just below the specimen surface, Figure 12.

A new high voltage cathode assembly was designed capable of providing rotational (or oscillational) motion to ensure uniform processing conditions (nitriding or film deposition). The cathode is introduced into the chamber through the central port of the top plate via a 3.8 cm ferrofluidic feedthrough. The feedthrough allows rotation of the specimen during processing without breaking vacuum and is controlled by a remote indexer enabling variable programming of the specimen motion. A pair of rubber o-rings embedded in the ferrofluidic feedthrough provides vacuum seal with the external grounded shield of the cathode assembly. A schematic representation of the cathode is shown in Figure 15. The cathode is composed of an external grounded stainless steel cylinder and an eccentric rod that carries the high voltage. A ceramic piece made out of machinable glass (Macor) provides electrical insulation between these two components. Also, a set of o-rings positioned between the grounded cylinder, high voltage rod and the ceramic piece provide vacuum seal as shown in Figure 15. The cathode is powered by a Hewlett Packard 6522A high voltage, low current power supply. The bottom end of the high voltage rod is threaded and can accept various sizes of specimen holders.
Figure 15  Detailed schematic of cathode assembly.
Temperature measurements is by optical pyrometry. The infrared ray was admitted through a barium flouride (BaF₂) window located on one of the angled ports onto the specimen surface. The infrared gun was calibrated by heating a nitrided specimen at various current densities, Figure 16. Finally, a shutter, introduced in the chamber from the top plate, exposes the specimen surface to the processing treatment when desired.

Various gases can be introduced into the chamber. Gas flow is controlled by two MKS mass-flow controllers (Type 1159) and monitored by an MKS Type 247C 4-channel readout that can also control ratios of gases admitted in the chamber. Vacuum level in the chamber is monitored by an MKS baratron Type 122A absolute pressure gauge powered by an MKS Type PDR-D-1 power supply with digital readout. In the lower region of the unit below the base plate, there are two thermocouple vacuum gauges to monitor pressure in the foreline to the diffusion pump and the bottom of the chamber. Vacuum in this system is maintained by a Varian NHS4 diffusion pump filled with DOW Corning 704 pump fluid and backed by an Alcatel 2030 mechanical pump capable of pumping 765 l min⁻¹.

Finally, the chamber has a central observation window and two inclined quartz glass windows facing the specimen surface used for optical measurements. A PC1000 computer-controlled fiber optic spectrometer manufactured by Ocean Optics is positioned in one of the optical windows to identify and measure the concentration of species (ions and neutrals) present in the plasma by emission spectroscopy.
Temperature, deg C

Cathodic Voltage: \( V_c = 2000 \) V
Emissivity: \( e = 0.48 \)

○ IPAP, \( p = 50 \) mTorr
□ Conventional Processing

\[ J, \text{mA cm}^{-2} \]

\( *p_1 = 90-100 \text{ mTorr}, p_2 = 160-170 \text{ mTorr}, p_3 = 240-250 \text{ mTorr} \)

Figure 16 Calibration chart of infrared gun.
B. Material

The substrate material selected for the present study was Ti-6Al-4V. The rationale for this selection was two-fold. First, nitrogen exhibits significant solubility in titanium (about 10 at.% at 500°C) and allows the study of diffusion processes during enhanced plasma treatments. Also, surface hardening of titanium alloys by nitriding is of significant technological interest. Titanium alloys exhibit a good combination of properties such as good strength, high fracture toughness and excellent corrosion resistance, but their tribological performance is unsatisfactory. Thus, surface treatments that have the potential to increase hardness and improve the wear resistance in this class of materials is of current interest. In the present study the titanium alloy was supplied by RMI Titanium in the form of an 18 mm diameter rod. Disc specimens 10 mm in diameter and 5 mm thick were machined, fine-ground and polished with 0.25 μm alumina as the final step. Prior to surface treatment the specimens were ultrasonically cleaned in methanol and dried in air.

Some preliminary work was also carried out on pure aluminum. However, the results for aluminum showed that this material was not a good model system for the present study, since nitrogen is not soluble in aluminum. Also, nitriding of aluminum under intensified plasma conditions showed that a thin nitride layer can form on the surface [15] but this layer cannot grow since the outward diffusion of Al is faster than that of N into the aluminum nitride. The results of the preliminary study are presented in Appendix I.
C. Processing

Three types of treatments were conducted during the course of the present work, nitriding, ion beam processing and sputter deposition, by using the IPAP processing system. Following polishing and cleaning, specimens were secured onto the specimen holder and then attached to the cathode rod. A standard procedure of elimination of contaminants in the chamber and on the specimen followed where the chamber was initially pumped down with the mechanical pump to about 0.1 Torr and then the diffusion pump was used to obtain a vacuum level of about $1 \times 10^{-5}$ Torr. The chamber was backfilled with Ar (99.99%) to 0.1 Torr and then pumped down again to $1 \times 10^{-5}$ Torr. This flushing process was performed to expel residual air (oxygen) and other gas contaminants. A glow discharge was evidenced by a uniform purple color plasma around the cathode during sputter cleaning. The system pressure was dynamically controlled at 0.05 Torr Ar pressure and the bias voltage slowly raised and maintained at 1 kV for 10 minutes or until a stable cathodic current was obtained.

For the nitriding treatments, after sputter cleaning the argon was gradually replaced with nitrogen and the desired operating pressure was maintained. Subsequently, the selected cathode voltage was applied and the positive electrode was biased at a positive potential in the range of 70 - 90 V. The purpose of the positive electrode is to attract and accelerate electrons increasing collisions and ionization in the plasma. A steady plasma current was achieved before turning on the electron emitting filament to intensify the plasma. The filament was initially turned on to a low intensity and then gradually increased to obtain the required cathode current density. The specimen was then processed for the selected period of time. At the completion of the
run, the filament was slowly turned off, followed by the power to the positive electrode and finally cathode voltage. The nitrogen was replaced again with Ar, the high vacuum valve was closed, and the specimen was allowed to cool slowly in the chamber to room temperature in the Ar atmosphere.

Ion beam treatments followed a similar initial cleaning procedure. After backfilling the chamber with Ar to the operational vacuum level (1x10^{-4} Torr), the desired voltage was applied and the appropriate gas (Ar or N\textsubscript{2}) was fed to the ion gun at the selected flow rate.

Thin films were deposited by magnetron sputter deposition. After sputter cleaning, N\textsubscript{2} (the reactive gas) was admitted in the chamber and the desired pressure (5-15 mTorr) was established. Then, the required voltage was applied first to the specimen (cathode) and then to the magnetron to sustain a plasma and sputter a Ti (99.999% purity) target resulting in deposition of TiN. The thickness sensor was used to monitor film thickness during deposition.

D. Characterization

Following treatment, specimens were evaluated by different methods depending upon the goal of the particular experiment. Surface analysis was carried out for elemental composition using AES. Chemical state and bond characteristics of compounds formed during treatment were analyzed using XPS. Microstructural and structural characterization were conducted by TEM. Surface morphology was studied by SEM and X-ray diffraction (XRD) analysis was used for obtaining crystal structure information.
1. Surface Analysis

The composition, chemical bonding states, and nitrogen depth profiles of processed specimens were investigated by AES and XPS. Sputter etching for depth profiling was carried out by 2 keV Ar<sup>+</sup> at 2x10<sup>-5</sup> Torr. AES analysis was accomplished with a 3 keV electron beam at a current of 40 μA. Relative intensities were determined from peak-to-peak heights and atomic concentrations calculated from these intensities by using the appropriate sensitivity factors. For titanium nitride analysis, the procedure described by Dawson and Tzatsov [97] was followed to circumvent the problem of overlapping peaks of the main KL<sub>23</sub>L<sub>23</sub> (378 eV) Auger emission from N with that of the L<sub>3</sub>M<sub>23</sub>M<sub>23</sub> (385 eV) emission from Ti.

For XPS, a 10 keV, 40 mA Mg-Kα X-ray source was utilized for photoelectron ejection from the specimen. The C1s at 284.6 eV was used as a reference for all detected peak positions. High resolution spectra were obtained in the binding energy range of interest for the various elements.

2. Transmission Electron Microscopy

Analytical TEM (JEOL 100 CX) at an accelerating voltage of 100 keV was utilized to observe the microstructural changes in the near-surface region of nitrided specimens. TEM foils from the near-surface region of the processed specimens were prepared using a dimple/grinder and a dual beam ion polishing system. Thin sections were first made parallel to the processed surfaces and then only the sectioned surface was polished. Specimen thickness of 100 μm was polished with 0.25 μm diamond
paste on a polishing wheel. The specimen was then fixed to a mount with a low melting point thermoplastic wax and mounted to a Gatan dimple grinder (Model 656 V3.1). The specimen was ground down to a thickness of about 20 μm prior to ion polishing. The final stage of specimen preparation was thinning the section using a Gatan precision ion polishing system (Model 691 PIPS V4.1). The thin section produced was then mounted on the TEM for analysis. In addition to microstructural characterization, electron diffraction (ED) was carried out to determine the structure of compounds formed as a result of IPAP processing.

3. Scanning Electron Microscopy

SEM was carried out on an ISI 60A scanning electron microscope to examine the surface morphology and appearance prior to and after processing. During preparation and prior to mounting in a low temperature epoxy resin, specimens were treated with an edgerment solution that results in a hard coating on the surface to ensure the edge retention during grinding and polishing. Metallographic cross sections polished to reveal the depth of the nitrided layer were observed by SEM to determine thickness and morphology of the modified layers and any changes along the depth of the specimen.

4. X-ray Diffraction

X-ray diffraction is one of the most effective ways to obtain crystal structure information. Crystal structures and lattice parameters of the produced nitrides were
studied by XRD to complement the ED analysis. Diffraction patterns were obtained from the bulk and near-surface region (low angle) of the films using filtered Cu-K\(_\alpha\) radiation with a wavelength of 1.54056 Å.

E. Property Assessment

Modification of the specimen surfaces after treatment was further characterized by examining the resulting properties. Microhardness measurements, wear, fatigue and corrosion testing were carried out to evaluate the effect of IPAP treatment on properties.

1. Microhardness Measurements

The formation of a nitride surface layer is expected to cause a major change in the surface hardness. Surface microhardness measurements were used to assess the effect of processing parameters on modified surface formation. Also, microhardness profiles of metallographic cross sections were used to determine the thickness of nitrided layers and obtain the depth of the nitrogen diffusion profiles. Knoop microhardness measurements were taken at various loads (25g-200g) of modified layers since this method is more sensitive to the shallow modified layers than Vicker's microhardness. A minimum of three indentations were made for each measurement to obtain statistically reliable hardness values.
2. Wear Resistance

Wear performance was evaluated by using a computer-controlled pin-on-disc tribometer (ISC-200 by Implant Sciences Corp.). The wear experiments were conducted in Ringer’s solution (simulated biological fluid) at room temperature at a loading level of 5 N and a sliding velocity of 0.1 m s\(^{-1}\) using PMMA pins (9.5 mm diameter) as the counterface material. First, experiments were conducted until steady-state was reached. Then long duration (30 km) experiments were conducted to assess the long term wear resistance of the produced surfaces. The coefficient of friction was monitored with the aid of a linear variable-displacement transducer. After testing, the wear rate was assessed by profilometry measurements on wear tracks and calculation of volume loss of the disc \(W_d\) material. Wear of the ball \(W_b\) was estimated by measuring the size of the wear scar using optical microscopy.

3. Fatigue Behavior

Fatigue crack initiation is a surface-sensitive property and therefore fatigue testing was carried out to evaluate changes caused by IPAP treatments. In order to observe pronounced fatigue crack initiation effects, “hourglass” fatigue specimens were used because their failure is surface-sensitive. The specimens had a midsection diameter of 0.28 in. Both IPAP-treated and untreated Ti-6Al-4V alloy specimens were tested at various stress amplitudes to establish S-N curves (stress amplitude-cycles to failure) and to determine differences in the fatigue response. An average value of the number of cycles to failure for three specimens tested at each stress level are reported.
These tests were conducted using an INSTRON (Model 8500) hydraulic testing machine. A pair of grips were used along with a special guide to allow alignment of the specimens. After attachment to the testing machine, the grips were vertically aligned by using Wood's metal reservoir. The tests were conducted at tension and full compression (R=-1) and at a frequency of 50Hz.

4. Corrosion Testing

Ti-base alloys have excellent corrosion resistance and hence, corrosion testing was carried out to determine whether that level of resistance is significantly affected after IPAP treatment. The corrosion behavior of processed surfaces was evaluated by carrying out anodic polarization tests using a computer controlled EG&G Corrosion Measurement System (Model 273). Disc specimens were mounted in epoxy, leaving only the processed area exposed to the environment, while electrical connection was obtained through a lead from the back side of the specimen. These tests were conducted in deaerated Ringer's solution (simulated biological fluid, approximately 0.1 M NaCl) at 36°C. The polarization scans started at a potential approximately 200 mV below the open circuit potential and progressed by increasing the potential at a rate of 0.5 mV s⁻¹. The polarization data were obtained in terms of corrosion current density vs. potential. Corrosion properties were obtained from the polarization response using a corrosion software (EG&G softcorr). All corrosion potentials were measured with respect to a saturated calomel electrode (SCE).
CHAPTER V. RESULTS AND DISCUSSION

A. Effect of Glow Discharge Intensification on Plasma/Solid Interaction

1. Sputtering Studies

1.1. Sputtering in Intensified Plasma Processing

Sputtering is a continual process that occurs during surface modification in plasma processes. When energetic particles strike a substrate, momentum is transferred to atoms of the substrate leading to various interactions depending upon the energy of the particles. For a cascade occurring close to the external surface, sufficient energy may be transferred to one or more atoms, so they are dislodged or sputtered from the surface. The penetration also causes a collision cascade leading to large numbers of atomic displacements producing numerous interstitials and vacancies. These processes have been extensively studied in the past for high energy ion implantation (E>10-100 keV). It is important to note that, low energy particles, such as those prevailing in plasma processes, can also produce defects to a depth of several atomic layers from the surface. However, there is very limited information on this issue in the literature and no systematic study has been previously conducted to investigate the sputtering process in this energy regime.

In the present study this aspect was investigated by conducting three series of experiments with average particle energy levels in the range of 100 to 1200 eV. The first set of experiments involved treatment of pure Si in an Ar plasma. In these experiments, part of the substrate surface was protected from the plasma and the
sputtering yield was measured by profilometry. An Ar plasma was employed in order to avoid reaction of the gas with the substrate and facilitate measurement of the sputtering effect. The second series of experiments involved sputtering tests of TiN using an Ar plasma. It is noted that during IPAP treatment of Ti, a thin TiN layer forms at the outer surface and thus, the sputtering process involves that layer. TiN films (~8μm) were deposited on Ti substrates by reactive magnetron sputtering (N plasma, Ti target). These experiments allowed the investigation of the variation of the sputtering yield as a function of particle energy and help identify possible critical energy levels beyond which defect formation becomes significant. Also, these results helped to investigate differences in energy requirements between sputtering of pure Si and TiN.

The third series of experiments involved sputtering of TiN by a nitrogen plasma as it occurs during nitriding. Besides sputtering, the nitrogen discharge in this case can also interact and remain in the near-surface region of the substrate modifying the sputtering process. Thus, these results were compared with the results from the second experimental series to obtain an understanding of the effect of nitrogen interaction (reaction, solubility, diffusion, etc.) with the substrate material on the sputtering process. The experimental values of sputtering yield were compared to theoretical estimations using the TRIM program [92] to develop an understanding of the near-surface effects during low energy particle bombardment.

The plasma parameters selected for the above three types of experiments are presented in Table 1. These parameters provided a systematic variation of ion and
Table 1: Surface modification parameters used in the sputtering experiments.

<table>
<thead>
<tr>
<th>Experimental Conditions</th>
<th>Cathode Voltage V</th>
<th>Current Density mA/cm²</th>
<th>Pressure mTorr</th>
<th>Sputtering Time hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>800</td>
<td>0.8</td>
<td>330</td>
<td>6</td>
</tr>
<tr>
<td>B</td>
<td>1700</td>
<td>0.8</td>
<td>190</td>
<td>4</td>
</tr>
<tr>
<td>C</td>
<td>1800</td>
<td>0.8</td>
<td>100</td>
<td>4</td>
</tr>
<tr>
<td>D</td>
<td>1500</td>
<td>0.8</td>
<td>50</td>
<td>2</td>
</tr>
<tr>
<td>E</td>
<td>2000</td>
<td>0.8</td>
<td>45</td>
<td>2</td>
</tr>
<tr>
<td>F</td>
<td>2000</td>
<td>0.8</td>
<td>30</td>
<td>1</td>
</tr>
<tr>
<td>G</td>
<td>2000</td>
<td>0.8</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>H</td>
<td>2000</td>
<td>1.0</td>
<td>20</td>
<td>1</td>
</tr>
</tbody>
</table>
Table 2: Fundamental plasma parameter values prevailing in sputtering experiments.

<table>
<thead>
<tr>
<th>Experimental Conditions</th>
<th>Ions</th>
<th>Neutrals</th>
<th>L/λ</th>
<th>Average Particle Energy * eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average Energy eV</td>
<td>No. of Ions</td>
<td>Average Energy eV</td>
<td>No. of Energetic Neutrals</td>
</tr>
<tr>
<td>A</td>
<td>100</td>
<td>5x10^15</td>
<td>50</td>
<td>6.9x10^16</td>
</tr>
<tr>
<td>B</td>
<td>200</td>
<td>5x10^15</td>
<td>100</td>
<td>7.0x10^16</td>
</tr>
<tr>
<td>C</td>
<td>400</td>
<td>5x10^15</td>
<td>180</td>
<td>4.0x10^16</td>
</tr>
<tr>
<td>D</td>
<td>600</td>
<td>5x10^15</td>
<td>270</td>
<td>1.66x10^16</td>
</tr>
<tr>
<td>E</td>
<td>800</td>
<td>5x10^15</td>
<td>325</td>
<td>1.8x10^16</td>
</tr>
<tr>
<td>F</td>
<td>1000</td>
<td>5x10^15</td>
<td>420</td>
<td>1.2x10^16</td>
</tr>
<tr>
<td>G</td>
<td>1200</td>
<td>5x10^15</td>
<td>500</td>
<td>8.0x10^15</td>
</tr>
<tr>
<td>H</td>
<td>1300</td>
<td>6.25x10^15</td>
<td>480</td>
<td>9.31x10^15</td>
</tr>
</tbody>
</table>

*$$E_{avg} = \frac{N_iE_i + N_nE_n}{N_i + N_n}$$*
neutral energies as shown in Table 2. Average ion and neutral energies were calculated using the equations outlined in section III.B.2.

### 1.2. Experimental Sputtering Yield Estimation

The sputtering measurements were conducted by masking part of the substrate surface from particle bombardment and recording the step developed between the masked and exposed surface after treatment by high resolution (5 nm) profilometry. Subsequently, sputter yields were calculated based on the sputtered volume. Figure 17 shows a typical measured step due to sputtering based on which sputter yield estimations were made (at least three measurements were conducted for each sputtering experiment). It should be noted that sputtering time was designed (Table 1) such as to allow development of a significant step size (a few microns) and reduce error. A sample calculation of the estimation of the depth of sputtering is shown in Appendix II.

Sputtering yield, $Y_s$, is defined as the number of substrate atoms ejected per bombarding particle. Experimental sputtering yield was estimated by assuming that the number of sputtered particles occupied the volume of material lost. Sputtering yield, $Y_s$, is thus expressed as:

$$Y_s = \frac{N_{sp}}{N_t}$$

(12)

where $N_{sp}$ is the number of sputtered atoms and $N_t$ is the total flux of incoming energetic particles. For the present work, the flux is composed of ions and energetic neutrals. A sample calculation of the experimental sputtering yield is presented in Appendix III.
Figure 17 A typical measured step of 8.8 μm created by Ar sputtering of TiN with $E_{\text{avg}} = 800$ eV.
Results of the experimental sputtering yield of Ar on Si, Ar on TiN and N on TiN are presented in Table 3.

1.3. Theoretical Predictions

Theoretical predictions of the sputtering yield of energetic particle bombardment on silicon and TiN were carried out utilizing the TRIM program.

The sputtering yield of highly energetic particles incident normally on the substrate has been derived by Sigmund [89] as:

\[
Y(E) = \frac{0.042 S_n(E) \alpha}{U_0}
\]  

where \( E \) is the average energy of incident particles, \( S_n(E) \) is the energy loss per unit distance by an energetic particle as it enters the substrate, \( U_0 \) is the binding energy of surface atoms equal to measured sublimation energy and, \( \alpha \) is a constant.

The sputtering yield of bombarding particles with energies in the range of or less than 1 keV has been shown by Bohdansky [90] expressed as:

\[
Y(E) = 0.0064 M_2 Y^{5/3} E^{1/4} \left(1 - \frac{E_{th}}{E}\right)^{7/2}
\]  

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Table 3: Experimental results of sputtering yield.

<table>
<thead>
<tr>
<th></th>
<th>Ar on Si</th>
<th>Ar on TiN</th>
<th>Nitrogen on TiN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Particle Energy, eV</td>
<td>Average Sputtering Yield, $Y_s$</td>
<td>Average Particle Energy, eV</td>
<td>Average Sputtering Yield, $Y_s$</td>
</tr>
<tr>
<td>55</td>
<td>0.024 ± 0.0022</td>
<td>205</td>
<td>0.094 ± 0.0029</td>
</tr>
<tr>
<td>110</td>
<td>0.053 ± 0.0116</td>
<td>300</td>
<td>0.141 ± 0.0076</td>
</tr>
<tr>
<td>205</td>
<td>0.126 ± 0.0087</td>
<td>345</td>
<td>0.139 ± 0.0158</td>
</tr>
<tr>
<td>345</td>
<td>0.139 ± 0.0158</td>
<td>430</td>
<td>0.135 ± 0.0068</td>
</tr>
<tr>
<td>430</td>
<td>0.135 ± 0.0068</td>
<td>490</td>
<td>0.144 ± 0.0193</td>
</tr>
<tr>
<td>590</td>
<td>0.144 ± 0.0193</td>
<td>590</td>
<td>0.260 ± 0.0145</td>
</tr>
<tr>
<td>770</td>
<td>0.260 ± 0.0145</td>
<td>810</td>
<td>0.292 ± 0.0200</td>
</tr>
<tr>
<td>810</td>
<td>0.270 ± 0.0135</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
where $E$ is the bombarding particle energy, $E_{th}$ is the threshold energy for sputtering to occur, $\gamma$ is the energy transfer function and $M_2$ is the mass of the target atom. The threshold energy can be approximated as:

$$E_{th} \equiv \frac{8U_0}{\left(\frac{M_1}{M_2}\right)^2}$$

(15)

where $M_1$ is the atomic mass of the incident particle. Also, the parameter $\gamma$ can be evaluated from the following relationship:

$$\gamma = \frac{4M_1M_2}{\left(M_1 + M_2\right)^2}$$

(16)

These expressions are used in the estimation of sputtering yield in the TRIM calculations.

Similar experimental conditions of ion and neutral flux ($L/\lambda$ values) and energies were used for the theoretical predictions as in the experimental studies, to allow a direct comparison. It should be noted that there are two fundamental differences between ion beam and plasma processes. The particle bombardment in the latter is conducted by ions and neutrals that exhibit a distribution in energy, whereas in ion beam sputtering there is a uniform energy level. Also, the plasma is made up of a
combination of ions and neutrals; therefore, due to charge exchange collision mechanism in the dark space, particle bombardment from varying angles takes place. Under the applied cathodic potential in the dark space, ions are expected to arrive at the substrate surface normally, whereas neutrals are expected to exhibit a variation in the angle of incidence, since they will not be affected by the electrical potential. It is possible that both of these effects can influence the sputtering process.

Figure 18 shows the change in sputtering yield as a function of particle angle of incidence and energy. Particles that incident the substrate normally (ions) are considered to have an angle of incidence of 0° whereas particles traveling parallel to the surface are considered to be 90° to the surface. Figure 18 shows that maximum sputtering occurs at ~75°. These results show that the angle effect is very small at low energies (E<200 eV) and it becomes significant only at higher energies (E>200 eV) and for angles > 35°. Examination of the charge exchange collision process in the dark space shows that the produced energetic neutrals are expected to exhibit a distribution in the angle of incidence that can vary from 0° to 90°. An average value of 45° was assumed for the neutrals. Thus, in the theoretical predictions, a 45° angle of incidence was used for the theoretical sputtering by neutrals and a 0° angle for ions. Table 4 shows the estimation of sputtering yield of Ar on silicon by TRIM calculations. Figure 19 shows the theoretical sputtering of silicon by Ar energetic particles as a function of energy. These estimations are for particle beams with a uniform particle energy for both the ions at 0° and neutrals at 45°. These results show a linearly increasing sputtering yield with particle energy in the range of interest.
Figure 18  Sputtering yield change as a function of angle of incidence and particle energy.
Table 4. Sputtering yield estimation of Ar sputtering on Si by TRIM.

<table>
<thead>
<tr>
<th>Experimental Conditions</th>
<th>Ions</th>
<th>Neutrals</th>
<th>L/(\lambda)</th>
<th>Avrg. Particle Energy, eV</th>
<th>Total Theoretical (Y_s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ion Energy, eV</td>
<td>(Y_{\text{si}})</td>
<td>Neutral Energy, eV</td>
<td>(Y_{\text{n}})</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>100</td>
<td>0.008</td>
<td>100</td>
<td>0.026</td>
<td>13.8</td>
</tr>
<tr>
<td>B</td>
<td>200</td>
<td>0.022</td>
<td>100</td>
<td>0.026</td>
<td>14.0</td>
</tr>
<tr>
<td>C</td>
<td>400</td>
<td>0.054</td>
<td>200</td>
<td>0.090</td>
<td>8.00</td>
</tr>
<tr>
<td>D</td>
<td>600</td>
<td>0.064</td>
<td>300</td>
<td>0.202</td>
<td>3.33</td>
</tr>
<tr>
<td>E</td>
<td>800</td>
<td>0.108</td>
<td>300</td>
<td>0.202</td>
<td>3.70</td>
</tr>
<tr>
<td>F</td>
<td>1000</td>
<td>0.126</td>
<td>400</td>
<td>0.260</td>
<td>2.40</td>
</tr>
<tr>
<td>G</td>
<td>1200</td>
<td>0.196</td>
<td>500</td>
<td>0.282</td>
<td>1.60</td>
</tr>
<tr>
<td>H</td>
<td>1300</td>
<td>0.200</td>
<td>500</td>
<td>0.282</td>
<td>1.50</td>
</tr>
</tbody>
</table>

Sublimation Energy = 4.643 eV
Figure 19  Theoretical sputtering yield of Si by Ar on Si.
As mentioned earlier, during the IPAP nitriding of Ti, a layer of TiN forms on the surface. Similar theoretical calculations of sputtering yield for Ar on TiN and N on TiN were carried out. Figure 20 shows the theoretical predictions for Ar particle sputtering of TiN. The theoretical predictions also show a continual increase in the sputtering yield with increasing particle energy. Also, the results suggest that some preferential N sputtering is likely. Theoretical predictions for N sputtering of TiN also show a similar trend as seen on Figure 21. Preferential sputtering of N is also suggested by these theoretical results. These calculations estimate only the sputtering yield and assume that the N energetic particles do not react with the substrate.

1.4. Discussion of Results

Figure 22 shows the experimental and theoretically expected sputtering yield of silicon in an Ar plasma. The theoretical yield was obtained by taking the average sputtering yield of ions and neutrals and their flux levels taking part at every energy level. The curve is not a linearly increasing one because it is the weighted average (flux level) of the different energies of ions and neutrals participating in the plasma. In general, sputtering under uniform energy of bombarding particles, produces a linearly increasing sputtering yield with energy as theoretically predicted, Figure 19, and experimentally observed. For example Ar ion beam experiments on Cu show that a linearly increasing region of sputtering yield exists for particle energies less than 1200 eV as shown in Figure 23 [112]. This is the region of interest under intensified plasma processing. The sputtering yield however decreases or levels off for particles with higher energies, as shown in Figure 24 [113]. The experimental yield was estimated
Figure 20  Theoretical sputtering yield of Ti and N by Ar on TiN.

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Figure 21 Theoretical sputtering yield of Ti and N by N on TiN (assuming no reaction).

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Figure 22: Experimental and theoretical sputtering yield of Si by Ar on Si.
Figure 23  Variation of sputtering yield with energy for Ar ions bombarding Cu (low energy) [112].
Figure 24  Variation of sputtering yield with energy for Ar ions bombarding Cu (high energy). The various curves are results of Ar ions bombarding Cu presented by different authors [113].
from the volume of particles sputtered as described in section V.A.1.2. The experimental results suggest the presence of three regimes in the sputtering process. It seems that there is reasonable agreement between experimental results and theoretical predictions in regimes I and III. Regime II initiates at about 200 eV average particle (ions and neutrals) energy and extends up to about 600 eV. Within this energy range sputtering rate seems to be substantially reduced and appears to be independent of energy level.

In regime I the experimental sputtering yield is observed to be higher than the theoretical. During estimation of the theoretical sputtering yield, the angle of incidence of the particles was considered as 0° for ions and 45° for neutrals. The angle of incidence of the neutrals in the plasma however, could have had more contribution from higher angle particles which have higher sputtering yield, resulting in the increased sputtering yield over the theoretical. Indeed, this may seem possible, since regime I refers to high \( L/\lambda >10 \) values (conventional) and has a higher pressure that results in higher density of lower energy particles. Under these conditions, more collisions take place within the dark space and it is possible that this process produces a somewhat higher angle of incidence. Calculations show that the two yielding rates in this regime are equal by an angle of incidence of about 52° which is not far from the angle assumed in the present calculations.

The substantially reduced sputtering yield in regime II, suggests that in this range of energy levels, the energy of the incoming particles contributes to other processes such as creation of defects in the near-surface region of the material. It is
interesting to note that in ion beam experiments, a change (reduction) in the slope of sputtering yield of Pt vs. ion energy of various inert gases (Ar, Xe, Ne) has been observed previously at 200 eV by Michely and Teichert [91]. It was suggested that at particle energies above 200 eV subsurface effects such as vacancy generation may start becoming significant compared to sputtering effects. The present results show that in the presence of a plasma (that involves also neutrals and an energy distribution for ions and neutrals) this regime is further pronounced and is expressed as a plateau rather than a change in the slope as observed in the previous ion beam experiments. Thus, the present results seem to suggest that under plasma conditions more beneficial effects such as defect generation can be realized. Fundamentally, these effects can be attributed to the modification of the collision cascade from the energetic bombardment under a combination of angle and energy variation. It is important to note that this is the first time that such effects are observed in plasma processes. Previous observations of these effects may have been difficult (or even impossible) to make in view of the low energies prevailing in conventional (low energy) plasma processes.

Figure 25 shows the experimental and theoretical sputtering yield of Ar on TiN. The theoretical curve was estimated in a similar manner as that in Figure 22. The experimental results in this case also have similar agreement in the low and high energy regimes as in Figure 22. The curve is essentially similar and made up of three regimes. This appears to be a general trend for plasma processes. However, regime II in Figure 25 seems to start at a higher energy level (~300 eV) than in the case of Ar on Si and extends up to ~550 eV. The energy level for the start of the plateau may indicate that a greater energy barrier is required for defect formation. Regime II in this case however,
Figure 25  Experimental and theoretical sputtering yield of TiN by Ar on TiN.
experiences an early rise in the sputtering rate. This can be attributed to the preferential sputtering of N from TiN that can produce a shorter plateau regime II.

Figure 26 shows the experimental and theoretical N sputtering of TiN. These results exhibit somewhat different behavior compared to that of Ar sputtering of TiN. First, the experimentally observed sputtering yield is significantly lower than the theoretically predicted for all energy levels studied. Second, the experimental behavior shows a linearly increasing sputtering yield without the presence of the regime II plateau. This behavior can be attributed to the reaction that takes place between the bombarding particles and the substrate producing a low sputtering yield. Also, this reaction can mask other physical processes (i.e. vacancy generation) that are taking place in the two earlier experiments (Ar on Si and Ar on TiN). The theoretical results show a similar behavior as in the Ar sputtering of Si and TiN. This similar effect stems from the fact that it is assumed that there is no reaction during the interaction of N on TiN.

Examination of the experimental results suggests that a threshold energy, $E_{th}$, of about $E_{th} = 175$ eV exists for sputtering of TiN in a nitrogen plasma. This threshold energy can be considered as the energy required to initiate sputtering, but also defect generation. This finding can provide an explanation to previous experimental observations that were reported. Ion nitriding studies on Ti as well as sputter-based deposition of TiN required a threshold energy between 100 - 150 eV for nitriding and effective deposition to occur [32,112]. However, no explanation was given for the existence of the identified threshold energy level. Additional work by Winters indicated that significant trapping of N in the lattice of the substrate occurred for bombarding
Figure 26  Experimental and theoretical sputtering yield of TiN by N on TiN.
particles with energies in excess of 150 eV [110]. Results of ion beam experiments by Wei et al. as shown in Figure 27 indicate that 304 stainless steel derived beneficial effects from "low" energy particle bombardment of N resulting in enhanced diffusion [30].

As some energetic particles (ions and neutrals) lose their energy to the target material to cause sputtering, others are embedded in the surface by implantation. The next section discusses the level of implantation that takes place and its significance.

2. Implantation Studies

Ion and/or neutral particle impact with a metal surface can cause sorption by two mechanisms. The particle can become physically trapped (implanted) in the lattice owing to its kinetic energy or it can dissociate with subsequent adsorption of the produced atoms on the surface [114]. Previous experimental studies have shown that such physical trapping via lattice penetration is quite improbable at energies below 100 - 150 eV [110]. The characteristics of implantation depth profile of energetic particles mainly depends on their energy of bombardment. Energy levels in IPAP (<1.2 keV) are significantly lower compared to those in ion implantation (5 to 1x10³ keV); therefore, implantation effects are expected to be in the range of several monolayers (<100 Å).

The energy of a particle approaching a metal surface is composed of three parts:

(i) the excitation energy which is represented by the ionization potential (for ions);

(ii) the interaction energy between the surface and the ion, and

(iii) kinetic energy (ions and neutrals).
Figure 27  Representative Auger-electron-spectroscopic (AES) N-concentration profiles in 304-stainless steel [30].

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Hagstrum [115, 116] has studied the mechanisms for neutralization of ions on metal and semiconductor surfaces and has found that the ions are neutralized into the ground electronic state of the molecule or atom via an efficient and rapid two-electron process at distances of ~5-6 Å from the surface. Upon arrival at the surface the N₂ molecules undergo collision-induced dissociation at the surface to yield two N atoms. The kinetic energy required for dissociation of N₂ has been determined to be about 9 eV [117]. It has been shown that among the three aforementioned energy components the kinetic energy of the bombarding particles is by far the largest and should be considered as the primary source for the activation energy of adsorption. It has been shown additionally that all of the existing data on N₂⁺ adsorption can be interpreted on the basis of a three step process where the ion is first neutralized, then dissociated upon impact with the surface and then the resulting atoms are absorbed on the impacted surface [98]. For energetic neutrals only the last two steps take place since they have been neutralized during charge exchange collisions in the plasma.

Previous N₂⁺ beam studies involving various nitride forming metals have demonstrated that nitrogen surface concentration (measured by XPS) mainly depends on the enthalpy of nitride formation, Figure 28 [118]. However, for a specific metal (e.g., Ti), the measurements showed that the amount of nitrogen on the surface was strongly dependent on ion dose up to a certain saturation dose and essentially was independent of kinetic energy over the range of 30-3000 eV [118, 119]. The N₂⁺ beam dose required to reach saturation has been determined to be 4x10¹⁶ ions cm⁻² which is easily attainable in plasma nitriding processes [119]. This energy independence of surface concentration
Figure 28  Plot of the enthalpy of formation of metal nitrides vs. the nitrogen (1s)/metal (2p_{3/2}) XPS intensity ratio for the first-row transition metals [118].
has been confirmed by others [98] and fostered by observations such that nitrogen adsorption was not affected by simultaneous surface damage caused by Ar\(^+\) beam bombardment [109]. Furthermore, experiments utilizing a N\(_2\)^+ beam on several metal surfaces showed that all probability of adsorption curves have a threshold around 9 eV and approach unity for energies at about 100 eV [117]. Thus, previous reports in the literature suggest that an energy level of \(~100\) eV may be required for significant adsorption to occur and adsorption may not be affected by particle kinetic energy for \(E>100\) eV. This condition is expected to be satisfied by a significant number of ions and energetic neutrals during the conventional plasma nitriding and thus adsorption is not expected to be a critical process in the present case. Thus, the reaction model by Lancaster and Rabalais [118] can be utilized to describe the adsorption process for N\(_2\)^+ and N\(_2\) particles with kinetic energies \(E_0 > 200\) eV and N\(^+\) and N particles with kinetic energies \(E_1 > 100\) eV:

Charge Exchange:

\[
N_2^+ (E_0) + e_m^- \rightarrow N_2 (E_0) g
\]

\[
N^+ (E_1) + e_m^- \rightarrow N (E_1) g
\]

Dissociation at Surface:

\[
N_2 (E_0) g + M_s \rightarrow 2N (E_0/2)
\]

Penetration of Atoms into Bulk:

\[
2N (E_0/2) + M \rightarrow N_b
\]

\[
N (E_1) + M \rightarrow N_b
\]

Chemical Reaction:
Ti + N → TiN; ΔH° = -180.5 kcal mol⁻¹

the subscripts M, g, s and b denote metal, gaseous, surface and bulk species, respectively.

Besides adsorption, nitrogen subsurface concentration (<100 Å) can be affected by implantation of energetic particles. Figure 29 shows the extent of Ar implantation into silicon as a function of particle energy. It can be noticed that a sharp concentration profile exists for Ar implantation at 200 eV at a depth of about 10 Å, whereas the concentration profile at higher energies (600 eV and 1200 eV) decreases in intensity and becomes broader. As particle energy is increased the maximum concentration is reduced, but the depth of implantation is increased. Peak implantation depth for particles with energy of 200 eV, 600 eV and 1200 eV, is about 10 Å, 20 Å and 35 Å, respectively. It should be also noticed that in all cases, in this energy regime, the profile does not extend beyond 100 Å. Similar trends are seen for Ar implantation into TiN as shown in Figure 30 and N implantation into TiN, Figure 31. Such implantation depth profiles have been experimentally verified [98].

In Ar implantation into TiN, the depth of implantation is reduced for all three energy levels compared to Ar implantation into Si target, but the intensity is increased. For energies of 200, 600 and 1200 eV the Ar implantation depth into TiN is about 8, 13 and 19 Å, respectively, compared to implantation depths of 10, 20 and 35 Å for Ar implantation into Si. The reduced Ar implantation into TiN is attributed to the denser nature of TiN (5.21 g cm⁻³) compared to that of silicon (2.32 g cm⁻³). The concentration
Figure 29  Theoretical predictions of Ar atom implantation into Si.
Figure 30 Theoretical predictions of Ar atom implantation into TiN.
of N implanted into TiN is reduced as compared to Ar into TiN, as shown in Figure 31, but the implantation depth is slightly increased. For example, at 200 eV N is implanted into TiN to a depth of about 10 Å with a peak intensity of about 0.074 atoms /Å/particle compared to Ar implantation into TiN to a depth of about 8 Å and a peak intensity of about 0.12 atoms Å⁻¹/particle⁻¹. The Ar atoms owing to their larger size migrate a shorter distance than the N atoms. Thus, Ar implantation results in shorter penetration, but a higher concentration.

Even though the depth of penetration is expected to be limited in the outer surface layer during implantation, the implanted particles may have indirect effects. For example, energetic particle impingement may increase the “sticking” probability (SP) at the surface compared to conventional low energy processes [114]. It has been found that sticking probability is low (~0.2-0.3) and almost independent of ion energy between 20 eV and 150 eV (energy regime prevailing in conventional process) [109]. Also, a thin nitrogen-rich layer can be generated from implantation that can serve as a nitrogen source especially in view of the fact that vacancies are mostly generated within that layer. There is evidence from previous work in our laboratory that very early in the nitriding process, high concentration of nitrogen is present at the surface [14]. In these experiments, plasma nitriding was carried out for a short period of time (5-15 min.). AES after nitriding revealed a 58 at.% N surface concentration. Ion beam experiments by other investigators also revealed a N/Ti surface ratio around 1.3 [98]. Calculations from the present implantation predictions, Figure 31, showed that an approximate concentration of 65 at.% N is expected in the outer surface layer during bombardment. These results seem to be in reasonable agreement with the experimental observations.
Figure 31 Theoretical predictions of N atom implantation into TiN (assuming no reaction).

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since some of the N is expected to migrate out after processing (either toward the surface or bulk) from this high concentration region during implantation.

Calculations based on the present predictions show that even though the implantation concentration profile characteristics (depth, atomic concentration distribution) change with energy, the overall concentration of N is not varied significantly within this energy regime. Simply beyond a critical energy level, all particles are embedded in the surface region. However, it should be noted that in these theoretical predictions only the energy of the impinging particles is considered and other indirect factors are not taken into consideration. In systems involving an exothermic reaction such as N and Ti, the state of the surface layer (e.g. presence of oxide from residual impurity oxygen), and sputtering effects can play a significant role. For example, during low energy plasma processing, more oxygen (impurity) is present due to higher operating pressure. Thus, oxide formation occurs more easily in the latter cases and a significant portion may remain at the surface region since the particle energy may not be sufficient to sputter it off the surface. For this reason, \( \text{H}_2 \) gas is utilized traditionally in the discharge of the conventional process in an effort to reduce the adherent surface oxide [32]. On the contrary, as particle energy in the plasma increases, oxygen contamination decreases (lower pressure) and oxide formation is limited. Also, in case that some oxide forms, it can be easily sputtered off due to the higher energies prevailing in the plasma.

Similarly, if resputtering effects are considered, it can be seen that the narrow and sharp profiles developed at low energy levels can be very sensitive to the sputtering process. For example, removal of an atomic layer from an implanted surface with 200
Figure 31, can reduce significantly (~25%-30%) the N concentration. Even though, sputtering yield will increase at higher energies, the concentration profiles are broader and have lower maximum concentrations and as such are less affected by sputtering. It has been reported that N trapping can start to be realized only for energies higher than 150 eV [110]. Thus, in view of the above results and discussion, implantation is expected to produce a nitrogen supersaturated layer at the near surface region. For energies higher than 150 eV, the nitrogen concentration is expected to show some variation with implantation energy. Similar effects have been previously reported for nitrided surface layers (WN) during nitrogen ion beam bombardment [110]. Exposure of W to N\textsubscript{2} (gas) produced a saturation coverage of about 6x10\textsuperscript{14} nitrogen atoms cm\textsuperscript{-2} (chemical adsorption), where bombardment with N\textsubscript{2}\textsuperscript{+} increased the coverage to ~1x10\textsuperscript{15} atoms cm\textsuperscript{-2} for all ion energies between ~20 eV and 150 eV (impact-activated adsorption). Above this energy level, increasing the ion energy to 300 eV and 450 eV, increased the saturation coverage to 8x10\textsuperscript{15} and 9x10\textsuperscript{15} atoms cm\textsuperscript{-2}, respectively (implantation effect). In agreement with these results, nitrogen surface concentrations during 500 eV and 2000 eV ion beam experiments on Ti surfaces were found to be within 10% [117]. Thus, above about 150-200 eV (where implantation effects can be realized) a nitrogen supersaturated surface layer forms with C\textsubscript{N} = 65 at.% N that can serve as an important nitrogen source and can interact with defects generated also at the near-surface region, significantly promoting diffusion processes. The present results show that implantation at this energy level can mainly increase near-surface region...
concentration and this energy level (150-200 eV) is at the threshold between the conventional and the intensified plasma process.

3. Diffusion Studies

Two comparative series of experiments were conducted to investigate the role of energetic particle bombardment on nitrogen diffusion. Parallel series of nitriding experiments using IPAP and ion implantation were performed. Two sets of conditions were used for the intensified plasma nitriding experiments. The parameters for the ion nitriding experiments were designed to produce ion energies comparable to those in ion implantation experiments. First, processing was performed at a pressure of 45 mTorr and by applying a cathode voltage of 2000 V in a pure nitrogen discharge. The thermionic emission system was activated to maintain a cathode current density of 2.4 mA cm\(^{-2}\). The second set of experiments was run at a pressure of 50 mTorr and a cathode voltage of 1500 V with a current density of 2.2 mA cm\(^{-2}\). Both conditions produced a substrate temperature of about 390°C. The total dose of energetic ions and neutrals was designed to be comparable to the total ion dose in the ion implantation experiments. Table 5 presents the average ion and energetic neutral energies along with their flux values for the above two sets of experiments as calculated by using the analysis of particle collision in the cathode dark space presented in the theoretical background section (III.B.2).

The nitrogen ion implantation experiments were conducted using a broad-beam N\(_2^+\) source (courtesy of Dr. P. Wilbur, Colorado State University). Specimens were
Table 5. Surface modification parameters for various treatments.

<table>
<thead>
<tr>
<th>Experim. No.</th>
<th>Method</th>
<th>Ion Dose x10(^{20}) ions/cm(^2)</th>
<th>Neutral Dose x10(^{20}) part./cm(^2)</th>
<th>Total Dose x10(^{20}) part./cm(^2)</th>
<th>Ion Energy eV</th>
<th>Neutral Energy eV</th>
<th>Processing Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ion Implantation</td>
<td>2.2</td>
<td>-</td>
<td>2.2</td>
<td>1150</td>
<td>-</td>
<td>117</td>
</tr>
<tr>
<td>2</td>
<td>Ion Implantation</td>
<td>0.79</td>
<td>-</td>
<td>0.79</td>
<td>1150</td>
<td>-</td>
<td>42</td>
</tr>
<tr>
<td>3</td>
<td>Ion Implantation</td>
<td>2.2</td>
<td>-</td>
<td>2.2</td>
<td>880</td>
<td>-</td>
<td>117</td>
</tr>
<tr>
<td>4</td>
<td>Ion Implantation</td>
<td>0.76</td>
<td>-</td>
<td>0.76</td>
<td>880</td>
<td>-</td>
<td>41</td>
</tr>
<tr>
<td>5</td>
<td>Ion Implantation</td>
<td>2.2</td>
<td>-</td>
<td>2.2</td>
<td>460</td>
<td>-</td>
<td>117</td>
</tr>
<tr>
<td>6</td>
<td>Intensified Ion Nitriding</td>
<td>0.8</td>
<td>1.7</td>
<td>2.5</td>
<td>1086(^*)</td>
<td>418(^+)</td>
<td>90</td>
</tr>
<tr>
<td>7</td>
<td>Intensified Ion Nitriding</td>
<td>0.72</td>
<td>1.78</td>
<td>2.5</td>
<td>761(^*)</td>
<td>297(^+)</td>
<td>86</td>
</tr>
</tbody>
</table>

\* Average ion energy  
\+ Average neutral energy
implanted with two different nitrogen ion doses of $2.2 \times 10^{20}$ ions cm$^{-2}$ and $0.78 \times 10^{20}$ ions cm$^{-2}$. The beam current was kept constant at $\sim 5$ mA cm$^{-2}$ producing a sample temperature of about $400^\circ$C. Specimens were ion implanted at three different ion energy levels: 1150 eV, 880 eV and 460 eV. The first two energies were selected to match the average ion energies used in the intensified plasma nitriding experiments. Similarly the two ion implantation doses employed are comparable to the ion and total dose employed in intensified plasma nitriding experiments (Table 5).

Compositional depth profiles were obtained by a combination of Ar$^+$ sputtering and microhardness measurements. Nitrogen content in the near surface region was determined by AES in conjunction with Ar$^+$ sputtering to obtain depth profiles. The method used to calculate N concentration from the Auger spectra is described in Ref. [97]. A sample calculation is presented in Appendix IV. The sputtering rate of TiN was obtained by using a standard stoichiometric film. The rate was determined to be 4 nm min$^{-1}$ and is in agreement with previous reports [98]. Microhardness tests of metallographic cross sections were performed to estimate the thickness of the compound layers and the depth of the nitrogen diffusion zone. A large difference exists between the microhardness of Ti$_2$N and N solid solution and that was used as the measure for determining the thickness of the Ti$_2$N layer.

3.1 Characterization

AES spectra taken from the surfaces of the ion implanted specimens showed nitrogen contents from 50 - 55 at.% depending on implantation energy. Also, XPS high
resolution spectra confirmed the presence of TiN at the outer surface layer of all implanted specimens. Figures 32 (a) and (b) present representative Auger and N 1s XPS spectra from ion implanted specimens, respectively. Figure 33 presents the compositional profiles of the specimens that were ion implanted at three different energy levels and two different ion doses. The AES spectra showed that a thin TiN (δ) layer is present at the outer surface of all implanted specimens followed by a thicker Ti$_2$N (ε) layer. Based on the measured sputtering rate of about 4 nm min$^{-1}$, the results show that Ti$_2$N is thicker than 0.25 μm. Also, the specimens implanted at higher energy exhibit hyperstoichiometric TiN surface layers and seem to show a Ti$_2$N layer somewhat richer in N compared to the specimens implanted at lower energies. These effects more than likely are related to the higher energy of nitrogen ions arriving at the surface that can be introduced into interstitial positions.

Intensified plasma nitriding of Ti-6Al-4V alloy produced very similar microstructures with those in the ion implanted specimens. Auger and XPS spectra showed that a hyperstoichiometric TiN layer is formed at the outer specimen surface followed by Ti$_2$N and an interstitial nitrogen diffusion zone. Figure 34 shows a typical Auger spectrum of an intensified plasma nitrided specimen (2000 V, 50 mTorr, 2.4 mA cm$^{-2}$). A TEM study was also conducted to obtain further insight of the microstructural characteristics of the produced near-surface layer. In this study, thin foils of nitrided specimens were prepared from the surface layer and region just below the surface layer as described in the experimental section. The TEM observations showed that the outer layer is composed of ultra-fine size (10-20 nm) δ-TiN grains, Figure 35. Selected area
Figure 32  Representative Auger and XPS spectra from ion implanted specimens.
Figure 33  AES nitrogen concentration profiles for various Ti-6A1-4V alloy specimens implanted with nitrogen ions at three different energies and two dose levels.
Figure 34  Typical Auger spectrum of intensified plasma nitrided specimen.
Figure 35  Bright field TEM micrograph showing characteristic TiN microstructure and corresponding diffraction pattern.
electron diffraction pattern analysis from this layer showed diffuse \{111\} rings suggesting lattice distortion and a preferred orientation along the \langle111\rangle direction, Figure 35. Evidence of lattice distortion was also present in TiN regions just below the outer surface as shown in the TEM micrograph in Figure 36 that was taken by using strain contrast. The above AES and TEM observations suggest that interstitial nitrogen is introduced in the TiN lattice under the intensified plasma conditions.

Figures 37 and 38 present the surface microhardness and microhardness profiles, respectively, for the ion implanted and intensified plasma nitrided specimens. It is clear that ion implantation and intensified plasma nitriding at the higher ion energy levels (>1100 eV) showed a significantly larger compound layer and longer nitrogen diffusion zone, while the compound layer for the specimens implanted or plasma nitrided at lower ion energies (<880 eV) is limited in the near-surface region. The plasma nitrided specimens show higher surface hardness than ion implanted specimens at comparable ion energy levels owing to the thicker compound layer. Table 6 presents the thickness of the produced layers for the various ion implantation experiments and the two intensified plasma nitriding experiments. As mentioned above, the nitriding treatments were designed to have their ion and total dose (ions and energetic neutrals) match the two ion doses of the same ion energy in the ion implantation experiments.

3.2 Diffusion Analysis

An analysis using a simplified multiphase diffusion model has been carried out to assess and compare the effective nitrogen diffusivities in the nitrided and nitrogen-diffused Ti-6Al-4V alloy surface layers formed by low-energy ion implantation and by
Figure 36  Bright field TEM micrograph showing significant distortion in TiN regions just below the outer surface layer.
Figure 37  Surface microhardness versus indentation load for various Ti-6Al-4V specimens implanted with nitrogen ions at three different energies and IPAP processed specimens.
Figure 38 Microhardness depth profiles for nitrogen ion implanted and IPAP processed Ti-6Al-4V specimens.

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Table 6. Thickness of various layers and calculated effective diffusivities of nitrogen in Ti-6Al-4V at 400° C.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Layer Thickness (μm)</th>
<th>Diffusivities (cm²/s)</th>
<th>Layer Thickness (μm)</th>
<th>Diffusivities (cm²/s)</th>
<th>Layer Thickness (μm)</th>
<th>Diffusivities (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TiN</td>
<td>Ti₂N</td>
<td>N Zone</td>
<td>TiN</td>
<td>Ti₂N</td>
<td>N Zone</td>
</tr>
<tr>
<td>1</td>
<td>0.03*</td>
<td>8.0</td>
<td>90</td>
<td>2x10⁻¹³</td>
<td>5x10⁻¹⁰</td>
<td>3x10⁻⁹</td>
</tr>
<tr>
<td>2</td>
<td>0.03*</td>
<td>4.4</td>
<td>45</td>
<td>9x10⁻¹³</td>
<td>2x10⁻⁹</td>
<td>2x10⁻⁹</td>
</tr>
<tr>
<td>3</td>
<td>0.02*</td>
<td>1.0+</td>
<td>30</td>
<td>1x10⁻¹³</td>
<td>1x10⁻¹⁰</td>
<td>3x10⁻¹⁰</td>
</tr>
<tr>
<td>4</td>
<td>0.02*</td>
<td>0.5+</td>
<td>20</td>
<td>3x10⁻¹³</td>
<td>8x10⁻¹¹</td>
<td>4x10⁻¹⁰</td>
</tr>
<tr>
<td>5</td>
<td>0.02*</td>
<td>1.0+</td>
<td>18</td>
<td>1x10⁻¹³</td>
<td>7x10⁻¹¹</td>
<td>1x10⁻¹⁰</td>
</tr>
<tr>
<td>6</td>
<td>2.6+</td>
<td>8.6</td>
<td>55</td>
<td>5x10⁻¹¹</td>
<td>2x10⁻⁹</td>
<td>3.4x10⁻⁹</td>
</tr>
<tr>
<td>7</td>
<td>0.5+</td>
<td>1.5+</td>
<td>20</td>
<td>5x10⁻¹²</td>
<td>2x10⁻¹⁰</td>
<td>2x10⁻¹⁰</td>
</tr>
</tbody>
</table>

Conventional Ion Nitriding

<table>
<thead>
<tr>
<th>800° C</th>
<th>400° C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2x10⁻¹²</td>
<td>7x10⁻¹⁷</td>
</tr>
<tr>
<td>2x10⁻¹⁰</td>
<td>7x10⁻¹⁵</td>
</tr>
<tr>
<td>4x10⁻¹¹</td>
<td>2x10⁻¹⁷</td>
</tr>
</tbody>
</table>

* estimated from AES depth profile
+ estimated from microhardness distribution
# these data have been calculated using the Arrhenius laws published in Ref. [101]
IPAP. The diffusivities deduced have also been compared with diffusivity data for nitrogen diffusion during conventional ion nitriding. Such an analysis and comparison is used to quantify the effects of energetic particle bombardment during ion implantation and IPAP on enhancing nitrogen penetration into Ti alloys.

As discussed above, three successive layers, TiN, Ti2N, and a nitrogen diffusion zone (solid solution), are present on surface-treated Ti alloy surfaces. As shown in ref. 14 for IPAP, generally these layers have well-defined interfaces between adjoining phases. The hardness and concentration profiles in Figures 37 and 38 suggest that this is also the case for nitrogen implanted and plasma processed samples. To estimate nitrogen diffusivities in these three layers, the following assumptions are made in the analysis:

(i) nitrogen is assumed to be the only diffusing species since the diffusion of Ti atoms is known to be orders of magnitude slower than the interstitial nitrogen [99];

(ii) nitrogen diffusivity is assumed to be independent of composition in a given phase;

(iii) thermodynamic equilibrium composition values, taken from published Ti-N phase diagram at the relevant temperatures, are used to approximate the compositions at the interfaces between adjacent layers;

(iv) the layer growth is diffusion-controlled; and

(v) the nitrogen concentration profile is assumed to be linear in each layer.
This last assumption has also been applied to the nitrogen diffusion zone composed of a solid solution. This may be only a crude approximation compared with a more-likely error-function type profile. However, considering the near-linear hardness profile observed (Fig. 38) and the fact that the nitrogen solubility is less than 10 at %, such an approximation is believed to be adequate for estimation purposes. It also allows a simple analytical treatment as it avoids the difficulties associated with numerically solving nonlinear equations if an error-function profile is adopted.

For the $i$th layer from the sample surface ($i=1$ for the first layer, TiN), the diffusing flux in the layer, according to Fick's first law, is

\[ J_i = D_i \frac{\Delta C_i}{L_i} \quad (17) \]

where $D_i$ is the nitrogen diffusivity in that layer, $\Delta C_i$ the concentration drop across the layer, and $L_i$ the thickness of the layer. The rate of thickness change for layer $i$, $dL_i / dt$, which can be determined from experimental data, can also be expressed as

\[ \frac{dL_i}{dt} = \frac{d(x_{i+1} - x_{i-1})}{dt} \quad (18) \]

where $x_{i+1}$ and $x_{i-1}$ are the positions of the two interfaces with the layers $i-1$ and $i+1$. The application of mass conservation at a given interface, e.g., interface $i-1 / i$, leads to
\[ \Delta C_{i-1/i} \frac{dx_{i-1/i}}{dt} = J_i - J_{i-1} \]  \hspace{1cm} (19)

where \( \Delta C_{i-1/i} \) is the difference of nitrogen concentration (in atoms cm\(^{-3}\)) across the \( i-1 / i \) interface. For the last layer, the nitrogen diffusion zone, the mass balance is established using the fact that all the nitrogen flux into the layer stays in the layer to build up the linear concentration profile. The treatment duration used in the experiments and the thickness of individual layers have been tabulated in Tables 5 and 6, respectively. Solving a set of equations with the above forms for three layers simultaneously, nitrogen diffusivities in the three layers for samples treated by ion implantation and IPAP can be calculated. The results are also tabulated in Table 6, together with diffusivities for conventional ion nitriding calculated from published Arrhenius laws [99]. Note that the latter laws are established for temperatures above 800°C only. In Table 6 values at 800°C and values obtained by extrapolation to 400°C are included.

### 3.3 Discussion of Results

From Table 6, it can be readily seen that nitrogen diffusion is greatly accelerated when intensified plasma (IPAP) or ion beam irradiation is utilized. The diffusivities are at least five orders of magnitude higher in these cases compared with conventional ion nitriding. In terms of temperature, the enhancement due to energetic particle bombardment is equivalent to a temperature increase of 400°C or more, because diffusivities with similar magnitude are expected only when ion nitriding temperature is
raised to above 800°C. It can also be seen that intensified plasma nitriding is almost as
effective as low-energy nitrogen implantation in enhancing nitrogen diffusivities. In
addition, compared with low-energy ion implantation, IPAP further enhances diffusion
in the top TiN layer (also see higher surface hardness in Fig. 37). This is likely due to
the fact that intensified plasma nitriding involves energetic neutrals in addition to
energetic ions. These neutrals apparently promote nitride formation. This is obvious
when comparing the thickness of the layers produced by intensified plasma nitriding
and nitrogen implantation with equivalent ion or total doses (Table 6). It is observed
that with equivalent ion dose to implantation, intensified plasma nitriding produces
compound layers of similar thickness, but a significantly thicker TiN top layer. The
results also suggest that the energetic neutrals do not have the same effect as ions in
enhancing nitrogen penetration beyond the top nitride layer(s). When the total dose in
intensified plasma nitriding (ions + neutrals) is equivalent to the total ion dose used for
implantation, the nitrogen penetration is considerably less in intensified plasma
nitriding.

Further insight into the intensified plasma nitriding process can be gained by
considering Figure 39 which illustrates the ion energy distribution prevailing during the
intensified plasma treatment based on the Davis and Vanderslice model. As has been
previously reported [12,62], the ratio $L/\lambda$ can describe the energetic particle distribution
in the dark space. For the high energy plasma treatment in the present experiments a
value of $L/\lambda = 2.19$ is obtained. The curve for $L/\lambda=10$ shown on the graph represents
the boundary between conventional ($L/\lambda>10$) and intensified ($L/\lambda<10$) plasma nitriding.
Figure 39  Ion energy distribution for the high ion energy ($E_i = 1086$ eV) IPAP nitriding treatment ($L/\lambda = 2.19$). The solid line ($L/\lambda = 10$) indicates the boundary between conventional and IPAP nitriding.
From the theoretical ion energy distribution it can be estimated that for an average ion energy $E_i^a = 1086$ eV, 47% of the ions have energies higher than $E_i^a$. In comparison, less than 2% of the ions will have energies higher than 1086 eV when $L/\lambda = 10$ (in fact average ion and neutral energies in this case are below 200 eV). Also, the total number of particles with $E > 1086$ eV is lower by two orders of magnitude compared to the intensified plasma.

In systems where a correlation between penetration depth and property enhancement exists, it has been shown experimentally [30] that an ion energy around 1 keV yields optimum effects on surface modification, although the reasons behind this observation are not entirely clear. The highest ion energy level used in the present ion implantation and IPAP experiments (1150 eV and 1086 eV, respectively) is within this energy range such that a pronounced effect on enhancing nitrogen diffusion is achieved. The possible existence of an optimal or threshold ion energy is supported by the observation that when implantation or IPAP energy is reduced ($E < 880$ eV), a significantly thinner nitride/nitrogen diffusion layer is obtained due to significantly lower diffusivities. This is consistent with the fact that there is no significant difference in the produced surface modification for the two low energy levels (880 and 460 eV), in spite of the significant difference in their implantation energy ($880 - 460 = 420$ eV).

The impact of the ionic bombardment can also be realized by considering the values shown in Table 6. The thickness of the produced layers during IPAP is similar to those of ion implantation when the ion dose rather than total dose (ions and energetic neutrals) of IPAP is taken equal to the implantation dose.
The present results are consistent with previous studies by Brokman and Tuler [9] showing that the local effective nitrogen diffusivity is proportional to the cathode current density. The role of ions has been hypothesized to lead to the generation of vacancies at the surface region and subsequent diffusion of vacancy-ion pairs [12]. It was suggested that the migration of such pairs into the bulk occurs by substitutional diffusion which can be much faster than the interstitial nitrogen atom diffusion [9]. However, the results of the present study show that in addition to the number of ions arriving at the cathode surface, their energy is also important with a critical level existing at about 1 keV. This critical energy level can be attributed to energy required to produce an optimal number of defects (vacancies or vacancy clusters) in the structure of the TiN surface layer that enhance the diffusion process.

4. Thin Film Deposition

In this part of the research, magnetron sputter deposition experiments were conducted where the particle energy was varied by varying the bias cathode voltage ($V_b$). Deposition of TiN thin films (about 900 Å thick) was carried out by nitrogen sputtering (2.1 sccm flow rate and 0.7 mTorr pressure) from a pure Ti (99.999%) target. The negative bias voltage was varied from $V_b = 0$ to -200 eV. Similarly, TiC and TiCN films were also deposited at various $V_b$ values in order to obtain a broader perspective of the reactive deposition process.

4.1 Film Characterization

Figure 40 presents the results on the N/Ti ratio as derived from the AES spectra analysis for TiNy films deposited at various substrate bias voltage values. The
Figure 40  Variation of stoichiometry of TiN films with substrate bias voltage.
stoichiometry was determined for the as-deposited films and after 2 min. of Ar$^+$ sputtering. It can be noted in Figure 40 that the N/Ti ratio of the as-deposited films varies with bias voltage ($V_b$). The films deposited beyond -120 V are stoichiometric, whereas films deposited at lower $|V_b|$ tend to have a ratio N/Ti>1. It is important to note that sputtering shows a dependence on substrate bias voltage. It is evident that films deposited at low $|V_b|$ show preferential nitrogen sputtering. This can be attributed to the incorporation of loosely bound nitrogen in these films (e.g. at grain boundaries [100]) that can be easily ejected by sputtering. Indeed such films possess a rather columnar structure and N can be easily incorporated into this type of microstructure. On the other hand, films deposited at $|V_b| > 120$ V are stoichiometric and show no significant variation in stoichiometry after sputtering. These results are also consistent with spectroscopic ellipsometry measurements taken from these films (as part of collaborative work with Aristotle University of Thessaloniki, Greece) [96].

The microhardness (Knoop at 25 g load) variation of the TiN$_x$ films as a function of $V_b$ is shown in Figure 41. It is evident that the film microhardness increases and reaches a plateau at a bias voltage of -120 V. This is in agreement with the AES results and consistent with the reasoning that at low $|V_b|$ some of the nitrogen resides at grain boundaries [100] and is not contributing effectively to hardness. This hardening response is also in agreement with TiN hardness values reported in previous studies [40]. A relatively larger hardness variation was observed for films deposited at -120 V more than likely due to the fact that -120 V lies in the lower boundary (transition region) of the plateau. Also, this variation was found to relate to the structure of these
Figure 41  Microhardness (Knoop at 25g) of TiN<sub>x</sub> films as a function of substrate bias voltage.
films. SEM observations showed that these films consisted of an island structure produced by a Stranski-Krastanov or mixed-mode film growth. Films deposited at -200 V exhibited high hardness probably due to denser structure and grain refinement produced under the enhanced plasma bombardment.

Another effect of resputtering is grain refinement. As |$V_b$| increases, the kinetic energy of the impinging ions and atoms increases resulting in enhanced surface mobility and destruction of the columnar structure thus, filling the valleys between columns and resulting in a fine-grained structure. In addition, defects induced by the impinging Ar' can serve as secondary nucleation sites [101] and along with the enhanced adatom mobility can result in grain refinement. Thus, as |$V_b$| is increased the gain size of the nitride is expected to decrease and this has been confirmed by TEM observations of film cross sections [102]. In addition, by increasing adatom mobility at elevated bias voltage levels, shadowing effects are eliminated and the porosity fraction in the film is decreased leading, generally, to a denser film [103], as shown in Figure 41 (i.e. -200 V).

In Figure 42 XRD patterns are presented for two TiN$_x$ films that were deposited at a bias of -80 V and -120 V. Calculations showed that the lattice parameter for the film deposited at -120 V was about 4.25 Å. Significant differences in the lattice parameter as a function of bias voltage of the TiN$_x$ films were not determined. The above value is within the range of lattice parameters reported earlier [42]. However, there were some characteristic differences in the appearance of the diffraction patterns with bias voltage. Figure 42 shows that as the absolute value of $V_b$ increases from -80
Figure 42  X-ray diffraction patterns of two TiN\textsubscript{y} films deposited at $V_b = -80$ V and $V_b = -120$ V.
to -120 V, the relative intensities of the (200) and (220) peaks increase, indicating the formation of a more random structure. The smaller degree of preferred orientation is consistent with the higher hardness value for this film, Figure 41. Also, the diffraction peaks at -120 V are sharper, probably owing to smaller lattice distortion. Both of the above effects can be attributed to the higher energetic Ar ion bombardment expected by increasing the absolute value of substrate bias and the lattice distortion induced by nitrogen in hyperstoichiometric films.

A summary of the results on TiC\(_x\) and TiC\(_x\)N\(_y\) films is given next. Figures 43 and 44 present the variation of TiC\(_x\) film C/Ti ratio and hardness as a function of the substrate bias voltage. The film stoichiometry was obtained after 2 min. Ar\(^+\) sputtering since the difference in the AES spectra between the carbon in TiC and carbon from surface contamination (i.e. vacuum system) is difficult to be discerned. It is evident from these results that the carbon content in the film increases with increasing |V\(_b\)| and reaches stoichiometry (x=1) at approximately -40 V bias. The hardness measurements show an increase with increasing stoichiometry that is consistent with previous observations [41]. XPS measurements from these films showed the presence of two peaks in the C 1s spectrum; a relatively sharp peak in the lower energy site corresponding to C in TiC (at about 281.5 eV) and a broad peak at 3 eV higher energy corresponding to C (from adsorbed hydrocarbon). Also, a shift to a higher binding energy was observed for the Ti 2p\(_{3/2}\) (at about 454.4 eV), indicating the presence of Ti in the chemical state of TiC.

The present results show that at |V\(_b\)| values close to 0 V, the TiC\(_x\) film is substoichiometric or it contains loosely bound C that can be easily sputtered off by Ar\(^+\).
Figure 43  Stoichiometry of TiC$_x$ films as a function of substrate bias voltage. The AES spectra were collected after 2 min of Ar$^+$ sputtering at 2 keV.
Figure 44  Microhardness (Knoop at 25 g) of TiC$_x$ films deposited at various substrate bias voltage values.
(Fig. 43). Since at $V_b = 0$ V the reaction probability of carbon at the substrate surface is very low, this indicates that during sputtering of the target substoichiometric TiC$_x$ is produced. When a bias voltage is applied, the plasma is activated allowing further reaction of sputtered carbon (C$^+$ or C') with TiC$_x$, thus increasing its stoichiometry. It is interesting to note that the stoichiometry in this case increases continuously in the bias range between 0 and -150 V, indicating that more than likely the reaction of carbon with sputtered titanium carbide molecules and ions occurs at the substrate surface.

Figure 45 presents the hardness variation of TiC$_x$N$_y$ films with nitrogen flow rate ($\Phi_{N_2}$) and substrate bias voltage. Since the hardness of TiC$_x$N$_y$ is higher than that of TiC, these results show that the bias voltage has a more significant effect than the nitrogen flow rate. XPS spectra from these films showed relatively broad C 1s and N 1s peaks indicative of a substoichiometric structure. Assuming again that the titanium carbide is sputtered from the target surface as substoichiometric carbide, then in a nonenergetic plasma (0 V) the reaction probability with nitrogen is very low. When the plasma is activated the reaction with nitrogen is promoted and is further enhanced as $\Phi_{N_2}$ is increased.

4.2 Discussion of Results

The present results show that a negative substrate voltage influences the stoichiometry and structure of all three types of sputter deposited films. The substrate bias was found to increase reaction probabilities of nitrogen owing to enhanced ionization and activation in the plasma by the applied bias voltage.
Figure 45 Microhardness (Knoop) of TiC\textsubscript{x}N\textsubscript{y} films as a function of N\textsubscript{2} flow rate and substrate bias.

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It has been established from previous studies [40] that under the present sputter deposition conditions, a stable thin δ-TiN phase forms due to nitrogen impingement and reaction with the target surface. It has been shown by previous mass spectroscopy results [104] that titanium nitride is mostly sputtered as titanium and nitrogen atoms and ions. Under these conditions, some reaction between N and Ti takes place but due to the low energy involved a significant portion of the nitrogen is loosely bound which upon sputtering would be easily removed and hardness will be low as was experimentally shown. An applied bias will increase the number of nitrogen ions in the plasma as well as their energy causing resputtering of the substrate surface. The ionization probability due to electron impact increases with electron energy and for most gases reaches a maximum at about 100 - 150 eV [105]. Thus, the increase in the resputtering with |V_b| accounts for the decrease in the nitrogen content with bias, Figure 40. The above justification is also consistent with the decrease in the deposition rates with increasing |V_b| as observed in the present study. For example, the deposition rate ranged from 5 Å s⁻¹ for V_b = 0 V to 2.5 Å s⁻¹ for V_b = -120 V. For a bias beyond about -120 V, the resputtering remains unchanged but the reaction probability of nitrogen increases due to higher energies involved promoting further reaction of nitrogen and increasing the amount of chemically bound nitrogen in the nitride. Since there is a reaction in this case, the stability and hardness of the compound produced is expected to increase as was experimentally observed.

The present results show that increasing the applied bias voltage increases the plasma energy and the reaction probability. Also, an energy barrier of about 120-150
eV exists that has to be overcome in order to form a dense compound with high stoichiometry at the substrate surface. It is important to note that during intensified plasma nitriding typical average ion and neutral energies are well above this level. Thus, in this case redeposition at the substrate surface is expected to maintain a stable TiN layer. On the contrary, during conventional ion nitriding only a small number of particles in the plasma would possess energies higher than this critical level and reaction with nitrogen will not be encouraged, thus producing significantly lower kinetics.

Similar observations have been made during ion plating, where a threshold energy ($eV^*$) also seems to exist, above which (considering factors as sputtering threshold) ‘effective’ ions are produced; this is likely to lie somewhere between 40 and 70 eV [95, 106, 107]. Similarly, the present evidence suggests that some equivalent threshold may also exist in plasma nitriding. It is interesting to note that Leyland et al [108], considering previous intensified nitriding work [63], data on nitriding adsorption on to metal surfaces [109,110] and dc diode discharge experiments where changes in the nitriding process with voltage were observed [111], suggested that this $eV^*$ threshold lies in the rage of 120-150 eV. It has been previously demonstrated that it is possible to produce effective nitriding by applying a bias cathode voltage as low as 200 V if plasma intensification is used [108,111]. However, nitriding under conventional diode conditions is often difficult at voltages <500 V. The reasons for this disparity lie with the different ion and neutral energy distributions in each case as mentioned earlier. The present results are in agreement with the above findings and further indicate (at least at this stage of the research) that this threshold may relate to resputtering and reaction probability effects which promote formation of a stable nitride at the substrate surface.
5. Modeling

5.1 Background of Model

As evidenced in earlier sections, under particle bombardment substrates undergo various physical processes which produce sputtering, implantation, structural defects and atomic displacement in the bulk and on the surface. Figure 46 is a schematic of the physical processes taking place in the near-surface region of the substrate. The implanted particles are initially within the near surface layer where other physical processes such as defect formation take place. Based on findings from the previous experimental sections, a modeling effort has been put forward to describe the nitriding process as it occurs during intensified plasma processing.

Sputtering was found to increase linearly with the energy of bombarding particles and thus sputtering yield, $Y_s$, can be described from results in Figure 26 as:

$$Y_s = -0.045 + 2.58 \times 10^{-4} E$$  \hspace{1cm} (20)

where $E$ is the average particle energy. The curve exhibits a threshold energy, $E_{th} = 175$ eV. The above expression can be modified to estimate the velocity, $v$ [cm s$^{-1}$] of the sputtering front as follows:

$$v = (-0.045 + 2.58 \times 10^{-4} E) \frac{N_s}{\rho_a}$$  \hspace{1cm} (21)
Figure 46 Interactions between incoming energetic atoms and substrate in the near-surface region.
where \( N_s \) [particles cm\(^{-2}\)s\(^{-1}\)] is the particle flux and \( \rho_{at} \) [atoms cm\(^{-3}\)] is the atomic density of the substrate.

In general, implantation is expected to increase N surface concentration. At the low energy end, the characteristics of the implantation profiles suggested that a threshold implantation energy of about 150-200 eV may be required to realize substantial physical trapping effects. Above this energy level, surface concentration can exhibit a minor increase with energy as has been observed [117], more than likely due to increases in sticking probability. Experimental evidence and theoretical calculations suggest that for the energy regime of interest, this concentration is about 65 at.% N and the layer thickness is <100 Å. The present results show that realization of sputtering (and associated vacancy generation) and implantation (resulting in higher surface concentrations) effects occurs at energy levels (150 - 200 eV) that consist the upper limit of the conventional plasma process and the low end of the intensified process. Thus, beneficial sputtering effects and a rich N surface concentration level may not be able to form during conventional low energy (\( E <200 \) eV) plasma nitriding.

Another related factor to be considered is the sticking probability. It has been established that the predominant species in the intensified plasma (\( L/\lambda <10 \)) is \( N_2^- \), whereas in conventional nitriding (\( L/\lambda >10 \)) the species is \( N^- \). Previous studies have demonstrated that for \( N_2^+ \) the SP = 0.2-0.3 for the regime between 20 eV - 150 eV and increases substantially above 150 eV [131]. It was suggested that the binding mechanism of \( N_2^+ \) is different involving impact-activated adsorption (in addition to chemisorption due to dissociation upon collision). Even though no studies with \( N^+ \)
plasma (prevailing at high pressure conventional nitriding) have been reported in the literature, the above results seem to suggest that the SP of $N^+$ would be lower than $N_2^-$ due to the absence of impact-activated adsorption. If this is indeed so, a much lower N surface concentration is expected in low energy plasma nitriding and this is in accord with current in situ Auger measurements [120]. Thus, in view of SP and implantation considerations, higher N surface concentrations are expected for $E > 150$ eV - 200 eV and this change can be associated with the energy level where the dominating species in the plasma is changing from $N^+$ to $N_2^-$ ($E \approx 200$ eV with $L/\lambda \approx 10$).

Energetic particle bombardment generates defects such as vacancies and interstitials. These vacancies that are generated either become annihilated in the near-surface region or diffuse into the bulk of the substrate. As suggested earlier by Brokman and Tuler [9], the vacancies can couple with arriving nitrogen atoms and diffuse substitutionally into the bulk of the material thus enhancing diffusivity. In this case a “stable” pair is formed between the negative effective charge of the vacancy and the positive effective charge of the N atom. The vacancy generation process was studied in the present research as a function of energy of bombarding particles. The theoretical predictions regarding defect generation under the energetic particle bombardment are summarized in Tables 7-9. These results show that there is no significant difference in the number of defects generated by neutrals owing to their different angle of incidence compared to ions of the same energy. Representative theoretical predictions of the depth and concentration of vacancies generated by N atom bombardment on TiN with energies of 200, 600 and 1200 eV are shown in Figure 47. It
Table 7. Theoretical predictions of defect generation by Ar in Si.

<table>
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<tr>
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<th>Vacancies, (vac/ion)</th>
<th>Target Displ., (atoms/ion)</th>
<th>Particle Energy, (eV)</th>
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Table 8. Theoretical predictions of defect generation by Ar in TiN.

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<th>Target Displ., (atoms/ion)</th>
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Table 9. Theoretical predictions of defect generation by N in TiN.

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Figure 47  Vacancy generation by N atoms in TiN.
is evident that very few vacancies, about 0.01 vacancies Å⁻¹particle⁻¹, are generated at a depth not exceeding 6-8 Å by bombarding atoms of 200 eV energy. However, particles with energies of 600 and 1200 eV generate about 0.25 vacancies Å⁻¹particle⁻¹ and 0.20 vacancies Å⁻¹particle⁻¹ at about a depth of 40 Å and 60 Å, respectively.

The present results (Table 9) show that a minimum kinetic energy of about 300 eV is required to initiate the vacancy generation process from the particle bombardment. It should be noted that upon impact dissociation, an N₂ particle with 300 eV will produce two N atoms each with ~150 eV energy and each N atom generating two vacancies. Furthermore, above this threshold level the vacancy profile concentration was found to exhibit similarities with that of particle implantation, in which low energy particles have a high and narrow bell-shaped peak and a lower and broader profile for higher energy particles. This point is illustrated in Figure 48 that shows the overlapping implantation and vacancy profiles for an energy level of 600 eV. It is evident that this combination creates an "interactive layer" where vacancies and N atoms can efficiently combine to enhance bulk N diffusion.

It should be pointed out that a large number of the vacancies generated by the energetic bombardment are expected to be annihilated. Obviously, as more vacancies are generated by increasing energy of incoming particles, the probability of coupling with a N atom increases. At a certain energy level, enough vacancies are expected to be present so each N atom can couple to a vacancy. Considering the results of the diffusion studies, this energy level for each N atom seems to be above 440 eV. It was determined that the diffusivity is significantly enhanced at bombarding N₂ particle energies above 880 eV. This would correspond to an energy of about 440 eV per N
Figure 48 Theoretical estimation of N vacancy generation and atom implantation depth in TiN.
atom. Table 9 indicates that about 7 vacancies are generated by each N atom at this energy level suggesting that more than 7 vacancies per N atom are required for successful coupling.

Figure 49 presents graphically the number of defects being generated by N atoms in TiN as a function of average particle energy. It shows a linear dependence of the number of defects on average particle energy. It is important to note that the actual vacancy concentration may be higher than that predicted theoretically since the present experimental results suggested that within a certain energy regime of the intensified plasma process (300 eV-650 eV) additional vacancy generation may take place. The N atom-vacancy interaction in the near-surface layer which contributes to the enhanced diffusion is modeled in the following section.

5.2 Model Description

Low energy ion bombardment has been shown by many researchers [121-125] to enhance diffusion by introducing a large concentration of point defects into the material. Similar effects have also been observed in plasma nitriding processes, where rf sources has been utilized to generate high ionization efficiencies [9, 126]. The previous and present studies suggest that similar physical processes take place during ion beam bombardment and particle bombardment in a plasma; however, energy and angular impact distributions should be considered. This is especially fostered by the fact that ions are discharged before they enter the material and in essence both processes involve neutral particle bombardment.
Defect generation by energetic N particles (N$_2^+$ or N$_2$) in TiN during IPAP.
Ion beam enhanced diffusion was mainly considered in microelectronic applications such as enhanced interdiffusion in heterojunction interfaces [127] and to enhance doping in extrinsic Si semiconductors [121]. For example, Lomer [128] has solved the basic equations for the enhanced diffusion coefficient considering the rates of point defect generation and annihilation under various conditions. Reviews in this subject can be found in Refs. 129 and 130. The most applicable model for the present case is the one based on the premise that the diffusivity in the affected layer is proportional to the concentration of vacancies as presented by Strack [121] and Eltoukhy and Greene [122].

Atom bombardment on a substrate surface results in a sputtering away of the surface at a velocity $v$ which is a function of particle energy. Saturation of the near surface region with $N$ atoms is achieved at a very early stage therefore attaining a steady state status. The production rate of vacancy-interstitial pairs is balanced by one or more of the following processes:

(i) radiation recombination of vacancies and interstitials,
(ii) thermally activated recombination,
(iii) annealing by diffusion to the surface or
(iv) diffusion to the bulk material.

The vacancy concentration $N_v$ at a distance, $x$, in a substrate experiencing diffusion of substitutional atoms is given as

$$N_v = N_n + N_0 \exp \left(-\frac{x}{L}\right)$$  \hspace{1cm} (22)
where $N_n$ represents the thermal equilibrium vacancy concentration and $N_0$ the excess concentration due to particle bombardment that depends on particle energy and $L$ is the diffusion length of vacancies. Considering the surface that moves with a constant velocity, $v$, Fick's second law gives:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) + v \frac{\partial C}{\partial x} \quad (23)$$

where $C = C(x, t)$ is the concentration of N. The initial conditions are $C_s = C(0, t)$ being the concentration at the surface which remains constant throughout the experiment and $C(x, 0) = 0$ being the concentration at time $t = 0$. For a vacancy diffusion mechanism, the diffusion coefficient is proportional to the vacancy concentration. Letting $D$ be the diffusion coefficient enhanced by the bombardment and $D_n$ being that for the thermally-activated diffusion, equation 22 can be expressed as:

$$\frac{D}{D_n} = 1 + \frac{[N_0 \exp(-x/L)]}{N_n} \quad (24)$$

By substituting $D_0 = N_0 D_n/N_n$ into Eqn. 24 the expression becomes:

$$D = D_n + D_0 \exp(-x/L) \quad (25)$$

The steady state solution for Eqn. 23 yields:
For the case of excess vacancies where $D_0 \exp(x/L) \gg D_n$ Eqn. 26 becomes:

$$C = C_S \exp\left\{ \frac{\left[ D_o + D_n \exp(x/L) \right]}{(D_o + D_n)} \right\}^{-vL/D_o} \quad (26)$$

Parameters $L$ and $D_0$ can be obtained graphically by writing the logarithmic derivative of equation 27 as:

$$\ln |d\ln C/dx| = \ln(v/D_0) + x/L \quad (28)$$

A plot of $\ln |d\ln C/dx|$ versus $x$ yields a straight line with a slope $1/L$ and an intercept $\ln(v/D_0)$. The velocity of the substrate surface $v$, is determined from Eqn. (21) above.

### 5.3 Model Verification

The above model was applied to experimental data that were obtained for plasma processing under two energy conditions. The first is representing intensified plasma nitriding and the second was lower energy plasma nitriding (approaching conventional processing). The average particle energy (ions and neutrals) of the intensified plasma was 450 eV and that of the lower energy process was 100 eV with a surface velocity of $v_1 = 2.9 \times 10^{-4} \mu m/s$ and $v_2 = 7.2 \times 10^{-5} \mu m/s$, respectively. Figure 50 shows the Auger profiles of the intensified and low energy processed specimens. Figures 51 and 52 present the logarithmic derivatives of the concentration profiles for
Figure 50  Auger profiles of intensified and low energy processed specimens [120]
Figure 51  Logarithmic derivative of N concentration profile for intensified plasma processing.
Figure 52 Logarithmic derivative of N concentration profile for low energy process.
these two experiments. The diffusivity of N, $D_N$, and diffusion length of vacancies, $L$, estimated from the intercept and slope of the curves under intensified and low energy conditions were found to be $D_{Ni} = 2.84 \times 10^{-12} \text{cm}^2 \text{s}^{-1}$, $L_1 = 156 \mu\text{m}$ and $D_{N2} = 3.57 \times 10^{-14} \text{cm}^2 \text{s}^{-1}$, $L_2 = 0.07 \mu\text{m}$, respectively. It is evident that plasma intensification produces a higher diffusivity and a longer diffusing length for vacancies. The diffusivity value is consistent with that determined in the diffusion studies section. It is interesting to note that even though the vacancy-N pairs seem to form in the near-surface region, they have long-reaching effects as evidenced by the deep nitrogen diffusion zones developed and predicted by the model. This can be attributed to the ability of N atoms to combine with vacancies and diffuse as a pair substitutionally which is much faster than the interstitial N diffusion [9]. This can provide an explanation for the long lasting effect of these defects as evidenced by the large value of $L$ compared to low energy process and also to regular substitutional diffusion such as B in Si during ion bombardment [121]. The coupling of N with the vacancy (as a result of attraction by the opposite effective charges) produces a “long lasting vacancy” because due to the presence of N atom, the vacancy is resisting annihilation. In other words, when an atom is attempting to jump to the vacant position, the presence of the N atom in the vicinity limits the success of the jumping process prolonging the life of the vacancy. On the contrary, B in Si is in substitutional positions and the vacancies are uncoupled to B atoms thus can be annihilated more easily in sinks and therefore $L$ exhibits low values as determined experimentally. Thus, the small size of N that is in interstitial positions, allows it to combine with a vacancy to form a pair. In conventional low energy process, simply the
concentration of vacancies is much smaller as predicted by the theoretical calculations, and their number is insufficient to combine with large enough N atoms, thus diffusivity remains low.

The present results show that diffusivity is expected to have an energy dependence since a higher vacancy concentration is expected with increasing energy. However, beyond a point where each N atom couples with a vacancy, the excess vacancies will not have any additional effect. In addition, the present findings can provide an explanation to previous experimental observations where a higher surface hardness was obtained when a mixture of argon-nitrogen discharge was used compared to pure nitrogen discharge [67]. As shown in Tables 8 and 9 more vacancies are produced by argon particles compared to nitrogen particles of the same energy. Thus, incorporation of Ar in the plasma has as a result the enhancement of the N diffusion that is translated into a longer diffusion depth and higher hardness.

B. Effect of Glow Discharge Intensification on Material Properties

Ti-base alloys exhibit an excellent combination of properties such as strength-to-weight ratio, corrosion resistance, fracture toughness and biocompatibility. However, they suffer in terms of wear, exhibiting galling that prevents their application in a wide range of engineering components. In the biomedical field specifically, Ti-base alloys are used for hip and knee replacements but a major drawback is their poor wear resistance. A need exists at present to improve the tribological performance of Ti-base alloys without causing significant reductions in other properties such as fatigue and
corrosion. The following sections present the property assessment of Ti-6Al-4V alloy produced after surface treatment under intensified conditions.

1. Microhardness Measurements

Surface hardness is of utmost importance in these materials, since high hardness directly relates to wear resistance. Significant improvements in the surface hardness of Ti-6Al-4V alloy were realized as a function of treatment time as shown in Figure 53. It is interesting to note that a three-fold increase in surface hardness was achieved over the unprocessed alloy ($H_K = 600$, 25 g) after a one hour treatment ($H_K = 1750$) under intensified processing conditions. Further treatment for 4 hr showed an even greater improvement in the surface hardness as a result of the thicker compound layer. An interesting observation during these treatments was that if a sufficient gap was present in the back side of the specimen (the back side of the specimen was not touching the surface of the holder), this side could also be nitrided as shown in Figure 54. The hardness on the back side was however lower than that of the front side. The reason for the observed nitriding is that nitrogen molecules can still reach the specimen surface by penetrating the space between the back specimen surface and the holder causing nitriding. The reason that the hardness of the front surface is higher is simply that the front of the specimen was interacting with both ions and neutrals, whereas the back surface was interacting only with neutrals. Thus, a higher flux of particles interacts with the front surface causing a higher hardness.

Surface roughness measurements showed that surface roughness is mainly a function of power density, Figure 55. It is evident that increasing particle energy will
Figure 53 Surface microhardness measurements for Ti-6Al-4V specimens processed under intensified conditions for different processing times.
Figure 54  Observed surface hardness on both front and back of processed specimens.
Figure 55  Surface roughness variation of Ti-6Al-4V with power density changes.

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have as an effect a greater level of impact, causing higher roughness. Also, for the same power density, it was observed that surface roughness increased with processing time as presented in Figure 56. A typical surface appearance of a Ti-6Al-4V alloy specimen after IPAP treatment is shown in Figure 57. These results show that proper selection of power density and time will be required to achieve a desired roughness.

2. Wear Resistance

Improvement of wear properties is a major concern for applications involving Ti-base alloys. In hip replacements, an area in which development of wear resistant Ti-base alloy surfaces is of utmost importance, the articulating parts involve a Ti alloy stem wearing against a PMMA cup while the system operates in muscle fluid. Thus, in the present study the wear tests were conducted by utilizing PMMA pins rubbing against intensified plasma nitrided Ti-6Al-4V surfaces in Ringer's solution (simulated body fluid). All testing was conducted at 5 N applied load and a sliding velocity of 0.1 m s⁻¹.

The results are presented in Table 10. By comparing Tests 1, 2 and 3, it is clear that nitriding by IPAP produces surfaces that possess a much higher wear resistance than those of untreated Ti-6Al-4V alloy (at least one order of magnitude lower wear rate). Another positive result was that IPAP nitriding was found to decrease the coefficient of friction (f) by 50%. The lower coefficient of friction is attributed to the ceramic nature of the nitrided surface (TiN) and the resulting surface strengthening. For the same loading level, substrate strengthening would reduce the contact area and produce a lower coefficient of friction. Also, for the present experimental parameters,
Figure 56 Surface roughness changes of Ti-6Al-4V with processing time.
Figure 57 Typical surface appearance of a Ti-6Al-4V alloy processed by IPAP for 2 hours (1 mA cm\(^2\), 2000 V), (a) overall appearance and (b) high magnification of (a).
<table>
<thead>
<tr>
<th>Test</th>
<th>Materials (Pin/Disk)</th>
<th>Sld. Dist./WT Dia. (km/mm)</th>
<th>Ball Scar, (mm)</th>
<th>W-T Width (mm)</th>
<th>W-T Depth (μm)</th>
<th>$f_{(f/f)}$</th>
<th>$W_D$ (x10^-3 mm³/Nm)</th>
<th>$W_P$ (x10^-5 mm³/Nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PMMA/Ti-6Al-4V</td>
<td>0.6/26</td>
<td>2.35</td>
<td>2.38</td>
<td>12</td>
<td>0.5</td>
<td>0.44</td>
<td>10.5</td>
</tr>
<tr>
<td>2</td>
<td>PMMA/Nitrided Ti-6Al-4V (2 h)</td>
<td>1/24</td>
<td>3</td>
<td>3.07</td>
<td>1.86</td>
<td>0.36/0.24</td>
<td>0.0201</td>
<td>16.7</td>
</tr>
<tr>
<td>3</td>
<td>PMMA/Nitrided Ti-6Al-4V (4 h)</td>
<td>1/24</td>
<td>2.9</td>
<td>3.27</td>
<td>0.71</td>
<td>0.34/0.24</td>
<td>0.018</td>
<td>14.6</td>
</tr>
<tr>
<td>4</td>
<td>PMMA/TiN Coating</td>
<td>30/27</td>
<td>8.0/8.5</td>
<td>4.23</td>
<td>2.2</td>
<td>0.5/0.2</td>
<td>3.46</td>
<td>4.15</td>
</tr>
<tr>
<td>5</td>
<td>PMMA/Nitrided Ti-6Al-4V (6 h)</td>
<td>30/24</td>
<td>4.5/4.5</td>
<td>1.75</td>
<td>0.7</td>
<td>0.3/0.22</td>
<td>0.21</td>
<td>0.2</td>
</tr>
</tbody>
</table>

PMMA pin diameter = 9.5 mm.
Results are averages of at least two tests per experimental condition.
there was no significant difference in the tribological behavior between the alloys processed for 2 and 4 hours. Thus, IPAP nitriding was found to cause significant improvements in the tribological properties of Ti-6Al-4V alloy surfaces.

Tests 4 and 5 are long duration tests (30 km) that were conducted to assess the long term durability of the produced surfaces. TiN-coated Ti-6Al-4V alloy was also tested for comparison purposes. It is interesting to note that the nitrided surface and the TiN coating have a similar coefficient of friction, but the wear rate of the nitrided alloy is at least one order of magnitude lower. This is attributed to the fact that nitriding results in a hardened layer that is developed within the structure of the material and as such is much more coherent compared to the TiN coating that has a columnar microstructure and a discrete interface with the substrate. Thus, significant improvements in wear behavior of Ti-6Al-4V can be expected by utilizing intensified plasma nitriding.

3. Fatigue Behavior

Surface modification methods have been used as a strengthening method to delay the onset of cracks during cyclic loading. In the present study, fatigue tests were carried out on hourglass specimens processed by the intensified conditions of IPAP. This particular type of specimens was used since they are very sensitive to fatigue crack initiation (failure occurs immediately upon crack initiation). The results of the fatigue study are presented in Figure 58. It is evident that the IPAP treatment has a beneficial effect on the fatigue behavior of the Ti-6Al-4V alloy. The fatigue life of the IPAP treated specimens was longer for all levels of stress amplitude. The results also suggest
Figure 58  S-N curves for IPAP-processed smooth Ti-6Al-4V fatigue specimens.
that at lower stress amplitude the improvement is larger. For example, fatigue testing at a stress level of 75 ksi shows that the IPAP treated specimen run out without failure while the untreated ones failed at about $1 \times 10^7$ cycles.

The achieved improvements in fatigue life of the IPAP treated Ti alloy are attributed to the strengthening of the surface region. The mechanism of fatigue crack initiation involves development of slip bands that under the reversible load produce extrusions and intrusions [130]. Strengthening of the surface region by IPAP nitriding increases the stress requirements for dislocation motion and slip band formation thus extending the fatigue crack initiation life.

4. Corrosion Testing

Figure 59 and Table 11 present the corrosion results of tests conducted in Ringer’s solution (simulated biological fluid) at 36° C. Besides unprocessed Ti-6Al-4V alloy and IPAP nitrided Ti-6Al-4V, TiN coated samples were also tested. The results showed that the presence of TiN either as a discrete coating or formed within the original structure of the substrate by IPAP, raises the corrosion potential ($E_{\text{corr}}$) by about 100 mV. The corrosion current density ($i_{\text{corr}}$) exhibited by the TiN coating was the lowest however all three current densities are considered very low. In agreement with that SEM examinations showed no evidence of any corrosion attack on specimen surfaces. Another factor that should be taken into account is that the current density was calculated by dividing by the nominal surface area and considering the larger surface area that exists in the IPAP specimen due to the higher roughness produced, the actual $i_{\text{corr}}$ should be considerably lower. Also, Figure 59 shows that the surfaces where TiN
Figure 59  Anodic polarization curves for TiN coating and Ti-6Al-4V substrate.

Table 11: Corrosion properties of Ti-6Al-4V-base materials in deaerated Ringer’s solution at 36°C.

<table>
<thead>
<tr>
<th>Property/Material</th>
<th>Ti-6Al-4V Alloy</th>
<th>TiN Coating</th>
<th>IPAP Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{corr}$ mV (SCE)</td>
<td>-355</td>
<td>-246</td>
<td>-233</td>
</tr>
<tr>
<td>$i_{corr}$ mA/cm²</td>
<td>0.14</td>
<td>0.03</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Values are averages of two tests

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was present (either TiN coating or TiN produced by IPAP) in general exhibited lower passive current densities. These results are in general agreement with previous reports on corrosion behavior of TiN coatings [10,11]. Nevertheless the present results demonstrate that IPAP treatment maintains the corrosion resistance of the material at the same more or less levels of the parent material. The apparent decline in the passivation tendency of the IPAP treated surface is because the nominal area is used for the calculation, but sputtering of the surface produces a larger effective area which is not actually known and therefore not considered in the estimation.
CHAPTER VI. CONCLUSIONS

The different physical processes taking place during plasma nitriding in the energy regime E<1200 eV have been studied to further understand the energetic bombardment effects during nitriding under intensified plasma conditions. The physical processes studied were sputtering, implantation, defect generation, diffusion and redeposition of sputtered material. The selected substrate material was Ti-6Al-4V alloy.

A. Sputtering Studies

Sputtering in an inert atmosphere was found to exhibit three regimes as a function of energy of the incoming particles. The first (low energy) and third (high energy) regimes agreed appreciably with theoretical predictions, while the second region showed a reduced level of sputtering yield that was rather independent of energy (plateau). The initiation energy and extent of the second regime depend on the type of bombarding particles and substrate material. The observed reduction in sputtering yield suggested that other bulk effects such as vacancy generation may take place in this energy range. Sputtering studies during nitriding showed that the effects of sputtering are overshadowed during this process as a result of the development of the nitride layer. The sputtering yield was found to increase linearly with the average energy of bombarding nitrogen. A threshold energy of about 175 eV was identified for the initiation of the sputtering process during plasma nitriding.
B. Implantation Studies

Implantation studies showed that in the energy regime of interest, N atoms are implanted to shallow depths (<80 Å) during intensified plasma processing. Implantation effects can be realized at particle energies >200 eV that can produce a N-rich surface layer that can serve as an important N diffusion source. Considerable vacancy concentrations can also be generated during implantation and the implantation and vacancy profiles are overlapping. Theoretical predictions showed that vacancy generation initiates at energies >~300 eV and experimental results suggested that a significant beneficial effect on diffusion by vacancies can be realized for N atom energies >440 eV. The present results show that the above energy levels are such that can hardly be attained during conventional plasma nitriding.

C. Diffusion Studies

The results of the diffusion studies showed that intensified plasma nitriding generates highly favorable plasma conditions compared to the conventional high pressure nitriding. Effective diffusivities prevailing in intensified plasma nitriding approach those in ion implantation for similar values of ionic flux and ion energies. The present diffusion analysis shows that energetic bombardment greatly enhances nitrogen diffusion into titanium nitride and solid solution layers. The present results show that the primary role in the intensified plasma process is played by the ions since they possess higher energies. The energetic neutrals (produced through collisions by the ions) are complementary by enhancing growth of surface nitride layers. Treatments with a critical ion energy level (~1 keV) lead to most effective enhancement.
D. Deposition Studies

The deposition studies showed that a negative substrate voltage can influence the stoichiometry and structure of sputter deposited TiN films. The bias effect can be explained mainly by enhanced plasma ionization and activation, producing resputtering effects and increasing reaction probabilities. The above processes result in grain refinement and the formation of denser and stable nitride structure at the near-surface region. A threshold energy was identified (about 150 eV) that is required for these beneficial processes to occur. In intensified plasma nitriding, the large majority of the energetic particles have energies well above this threshold energy, whereas in conventional plasma nitriding only a very small fraction usually exceeds this energy barrier. The present results show that considering energies that prevail in the intensified plasma, formation of stable TiN is expected and is maintained during processing at the outer surface layer, as has been experimentally verified.

E. Model

A model was developed to describe the nitriding process under intensified glow discharge. The model is based on the premise that a considerable vacancy concentration is developed in the near-surface region under the energetic bombardment and the N diffusivity is proportional to the vacancy concentration. Also, the produced vacancies are coupling with N atoms resulting in long-lasting pairs that migrate by substitutional diffusion. The model was experimentally verified and the diffusion length of vacancies was found to be significantly higher under the intensified condition (156 μm vs. 0.1 μm

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for the conventional process). The present results suggest that vacancies can migrate to significant depths since while coupled with N atoms their probability of annihilation is reduced and therefore contribute effectively towards atomic diffusion of N resulting in higher diffusivities.

F. Properties of Modified Surfaces

An assessment of surface-sensitive engineering properties showed that significant improvements can be achieved by intensified plasma nitriding. More specifically, the surfaces produced exhibited significant improvements in hardness, wear resistance and fatigue crack initiation. All these improvements were realized without adversely affecting the corrosion resistance of the original substrate material. The present results show that intensified plasma nitriding can produce new surface characteristics in Ti-base alloys and expand their field of engineering applications.
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120. V. Palshin and E.I. Meletis, unpublished results.


APPENDICES

Appendix 1

Nitriding of Aluminum

Commercial 6061 Al alloy (wt.%: 1.0 Mg, 0.6 Si, 0.28 Mn, 0.2 Cr, balance Al) was used in the present study as the substrate material. Disc specimens of 20 mm in diameter and 2 mm thick were prepared. The discs were ground and polished through 0.25 μm diamond paste and ultrasonically cleaned in acetone before plasma processing.

Conventional nitriding was achieved with a substrate negative bias of 600 V and a pressure of 1.5 Torr. The cathode current density during these experiments was 0.58 mA cm$^{-2}$. The intensified plasma experiments were carried out in a similar manner as described above, except at lower pressures and higher current densities. The specimens were first sputter-cleaned at a substrate bias voltage of 2000 V and an Ar pressure of 45 mTorr for 10 min. Pure N$_2$ gas was then introduced for nitriding and dynamically maintained at the desired pressure for each experiment. Two intensified plasma experiments were conducted and were designed such as to cover a high and a low level of the plasma energy spectrum of the process. The cathode voltage, cathode current density and pressure used for these two sets of experiments were: (i) 2000 V, 2.4 mA cm$^{-2}$, 50 mTorr, and (ii) 800 V, 1 mA cm$^{-2}$, 100 mTorr, respectively. All nitriding experiments were conducted for 2 hr at a temperature of about 400° C.

1. AES and XPS Analysis

AES analysis after nitriding showed mainly the presence of Al, N and O in all processed specimen surfaces. Sputtering for a couple of minutes with Ar$^+$ reduced the
amount of O significantly, however, $\text{Al}_2\text{O}_3$ was still present at the surface region. The spectra from the two intensified plasma experiments were very similar but they exhibited differences with those obtained from specimens treated by conventional plasma nitriding. Figure 60 presents the main characteristic peaks after 2 min. sputtering for specimens treated by using the two processes. As observed in the figure, the Al (LVV) peak shows a shift from 68 eV for pure Al to 60 eV and 56 eV for intensified plasma and conventional nitriding, respectively. Similarly, the Al (KLL) peak is shifted from 1399 eV for pure Al to 1386 eV for IPAP and is virtually non-existent for the conventional process. In the latter case the observable Al (KLL) peaks appear at 1300 eV and 1350 eV. Also, the positive section of the N (KLL) peak for intensified plasma nitriding is more pronounced compared to that for the conventional process. These chemical shifts of 8-13 eV to lower energies and the changes in the signal shape from pure Al clearly indicate the formation of nitrides as has been documented previously [24]. The shift in energy levels and changes detected are consistent with the formation of AlN during conventional plasma nitriding [24,131,132] and an Al$_3$N chemical state for intensified plasma [15]. Depth profiling showed that a compound with an approximate stoichiometry of Al$_3$N forms with IPAP treatments. The thickness of the Al$_3$N layer was estimated to be in the submicron range.

XPS spectra of the Al 2p, N 1s and O 1s showed broad peaks indicating the presence of more than one chemical state for Al. The Al 2p spectra for example showed peaks at 73.8 eV and 74.6 eV. The shifts in the binding energies were consistent with the presence of aluminum nitride and $\text{Al}_2\text{O}_3$ at the surface region [15,24]. Similarly,
Figure 60  Auger spectra for specimens treated with IPAP and conventional ion nitriding showing the Al (LVV), N (KLL), O (KLL) and Al (KLL) transitions after 2 min sputtering.
shifts in the binding energies of N and O 1s peaks were detected consistent with the formation of aluminum nitride and oxide.

2. Microstructural Characteristics

The aluminum nitride layer formed using conventional nitriding exhibited a dark black color whereas intensified plasma nitriding produced a lighter black color. Also, the aluminum nitride layer developed by conventional nitriding showed signs of detachment whereas high and low energy plasma IPAP produced adherent and uniform layers. Figure 61 presents SEM micrographs showing typical surface appearance for these layers. It has been reported [131,132] that using the conventional method suitable nitriding can be achieved only at high temperatures in the range of 480±20° C. On the other hand, if the nitriding temperature is lower as in the present study (400° C), the conventional method cannot produce adherent and uniform nitride layers. Furthermore, AlN layers developed previously by conventional plasma nitriding showed distortion which resulted in microcracks and macro scaling consistent with the present results [131,132]. This has been attributed to the development of significant compressive thermal stresses (2000 - 3000 MPa) owing to differences in the thermal expansion coefficients between the AlN layer and the Al substrate. Another reason is the significant volume expansion associated with the formation of AlN as has been reported by Meletis and Yan [15]. Adherent aluminum nitride layers were developed by IPAP because the layers were composed mainly of Al₃N. Under the energetic bombardment prevailing in IPAP formation of the metastable Al₃N is promoted. Thus, an adherent layer forms since significant thermal stresses are not developed. It should be noted, that
Figure 61  SEM micrographs showing surface morphology of specimens produced by (a) high plasma energy IPAP and (b) conventional ion nitriding. In the right hand side of the micrograph the AlN film has been detached.
during conventional nitriding the higher processing temperature provides the energy required for the formation of the equilibrium AlN phase. Similarly, formation of the equilibrium phase occurs in nitrogen ion implantation since significantly higher energies exist compared to IPAP [18,24].

A nodular morphology was evident on all nitrided surfaces. This type of particle growth tends to suggest that significant outward diffusion of Al occurs and reaction with N takes place close to the outer surface, thus, a nodular nitride shape is developed to minimize surface energy. This nodular morphology would not have been expected if the process were dominated by inward diffusion of N producing an internal nitride growth. There is also indirect evidence supporting the above suggestion. Thick aluminum nitrided layers were produced in Al substrates when a nitrogen ion implantation treatment was performed prior to plasma nitriding [26]. Nitrogen ion implantation is producing AlN below the surface that acts as a barrier to outward diffusion of Al but allows the inward diffusion of N and the subsequent in-growth of the nitride. The growth in areas close to the edge of the specimens treated with high plasma energy during IPAP showed smoother surfaces, Figure 62. This more than likely is the result of more intensive sputtering along the edges owing to higher currents at these sites.

TEM observations made on nitrided specimens showed the presence of very fine microstructures. Specimens treated by IPAP showed the presence of a dense and fine microstructure with a face centered cubic (fcc) structure with an approximate grain size of 5-10 nm, Figure 63. The lattice parameter of the nitride was determined to be close to 4.38 Å. This nitride can be thought of as forming by an expansion of the original fcc
Figure 62  SEM micrograph showing an area close to the edge of a specimen nitrided by high plasma energy IPAP.
Figure 63  
(a) Bright field TEM showing microstructure of Al₃N synthesized by IPAP and (b) diffraction pattern from area shown in (a).
Al structure due to the incorporation of N in the unit cell. The diffraction patterns also showed that some AlN may be present, consistent with the light black color observed by SEM on the surface of these specimens. The \( d \)-spacing for the (111) Al\(_3\)N and (00.2) AlN reflections are very close (2.52 Å and 2.48 Å, respectively) and both of these may contribute to the first diffraction ring, Figure 63. Specimens treated by conventional nitriding showed the presence of the hexagonal AlN phase, Figure 64. The \( d \) space analysis was in agreement with the only stable aluminum nitride that has been observed in the AlN phase diagram with the hexagonal ZnS (wurtzite type) structure and lattice parameters of \( a = 3.11 \) Å and \( c = 4.98 \) Å. The AlN film showed significant porosity and a round shape of that phase was evident, Figure 64(a). Dark field image analysis showed that the size of the AlN particles was on the order of 15-30 nm, Figure 64(c). This size is consistent with the presence of the diffuse ring from the (00.2) diffraction of the AlN phase, Figure 64(b). Furthermore, the electron diffraction pattern showed that some large intermetallic Mg\(_2\)Si precipitates were still present even after nitriding (most inner ring in the diffraction pattern).

3. Hardness of Modified Surfaces

Figure 65 presents the microhardness measurements for the surfaces processed by IPAP. Attempts to take measurements from nitrided surfaces using the conventional method were unsuccessful since the nitride layer was flaking off. Similar cracking of AlN layers developed by conventional plasma nitriding has been reported to occur instantly in scratch tests by using a diamond indenter [131]. Microhardness measurements from specimen surfaces treated by IPAP showed that a three-fold increase in hardness can be achieved by this method. Furthermore, it is interesting to
Figure 64  (a) Bright field TEM showing microstructure of AlN synthesized by plasma nitriding; (b) electron diffraction pattern of area shown in (a) and (c) dark field image by using a section of the (00.2) diffuse ring, which is the second ring shown in (b) corresponding to the AlN phase. The inner ring corresponds to the Mg$_2$Si precipitates.
Figure 65  Surface microhardness measurements as a function of load for specimens nitrided with low and high energy plasma IPAP.
note that the surface hardness increased with increasing the energy of the plasma. This can be attributed to the development of a thicker nitride layer under the IPAP treatment with higher plasma energy. It has been shown previously that higher energy bombardment critically affects the generation of defects and vacancies at the near-surface region that subsequently enhances diffusion processes and growth kinetics [12-14, 93].

4. Corrosion Behavior

The anodic polarization curves for IPAP-treated and untreated 6061 Al alloy are shown in Figure 66. The current density developed during testing of the specimens processed with conventional nitriding were several orders of magnitude higher and thus are not shown on the graph. Post-testing examination of the latter specimens showed that the AlN film was completely dissolved and the aluminum substrate exposed. The IPAP-treated and untreated Al alloy specimens exhibited very similar corrosion potentials and a corrosion rate of 26 mA cm$^{-2}$ and 7.5 mA cm$^{-2}$, respectively. Even though the IPAP treatment caused an increase in the corrosion rate the actual value still remains very low. This increase can be attributed to the activation of the surface caused by IPAP and introduction of defects due to energetic bombardment. However, the nitride layer remained at the surface after corrosion testing and surface examination showed no evidence of any serious corrosion attack.

5. Concluding Remarks

Table 12 presents various plasma parameters existing during IPAP and conventional nitriding. These parameters were estimated by using a theoretical
Figure 66 Anodic polarization curves of IPAP treated (high energy plasma) and untreated 6061 Al alloy in 0.1 M NaCl solution.

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Table 12: Estimated plasma parameters during IPAP and conventional ion nitriding of aluminum.

<table>
<thead>
<tr>
<th>Process Type</th>
<th>Ions, ( N_i ) (m(^2)s(^{-1}))</th>
<th>Average Ion Energy, ( E_{i*} ) (eV)</th>
<th>Energetic Neutrals, ( N_n ) (m(^2)s(^{-1}))</th>
<th>Average Neutral Energy, ( E_{n*} ) (eV)</th>
<th>Average* Particle Energy, ( E_{p*} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPAP #1</td>
<td>1.5x10(^{28})</td>
<td>1029</td>
<td>3.57x10(^{20})</td>
<td>400</td>
<td>586</td>
</tr>
<tr>
<td>High Energy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IPAP #2</td>
<td>6.08x10(^{19})</td>
<td>554</td>
<td>2.31x10(^{20})</td>
<td>65</td>
<td>167</td>
</tr>
<tr>
<td>Low Energy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conventional Nitriding</td>
<td>3.62x10(^{19})</td>
<td>20</td>
<td>2.16x10(^{21})</td>
<td>8</td>
<td>8</td>
</tr>
</tbody>
</table>

\( E_{p*} = (N_i E_{i*} + N_n E_{n*})/(N_i + N_n) \)
treatment that has been described previously [12]. It is evident that significantly higher ion and neutral energies prevail during IPAP compared to conventional plasma nitriding. The energetic bombardment during IPAP produces significant N penetration that consequently results in the formation of highly adherent and metastable aluminum nitride which uniformly covers the surface [93]. A significant AlN layer cannot be sustained at the surface due to continuous sputtering from the energetic bombardment. Conventional ion nitriding on the other hand can result in the formation AlN after prolonged sputter cleaning but the layer is porous and not adherent. The loosely bound layer could be a result of outward diffusion of AlN which reacted with the nitrogen to form an outward layer. On the contrary, the higher energetic N flux prevailing during IPAP can result in significant N penetration thus reducing the outgrowth of the nitride and enhancing its inward formation for a limited depth. The nitride in this case cannot grow any further more than likely due to low diffusivity of nitrogen in the nitride and the concurrent high sputtering rate prevailing during intensified plasma nitriding.

6. References


Appendix 2

Sample Calculation of Depth of Sputtering: Argon on Silicon

This estimate was carried out using the TRIM program.

Nitriding Conditions

Cathode Voltage, $V_c = 2000$ V  
Pressure, $p = 50$ mTorr  
Time, $t = 1$ h  
Current Density, $J = 1$ mA cm$^{-2} = 10$ A m$^{-2}$  
$L/\lambda = 1.49$

Energy of Bombarding Particles

Average Ion energy $E_i^{a} = 1290$ eV  
Average Neutral energy $E_n^{a} = 476$ eV

Ion Flux

The ion flux $N_i$ is given as:  
$N_i = J_{\text{eff}}/q$

where, $q =$ the ionic charge and

$J_{\text{eff}} =$ the effective current density which is equal to $J_{\text{eff}} = J/(1+\gamma)$.  
$J =$ the measured current density and $\gamma =$ the secondary emission coefficient.  
However, $\gamma =$ negligible and therefore

$N_i = J/q = 10/1.6x10^{-19} = 6.25x10^{19}$ ions m$^{-2}$ s$^{-1} = 6.25x10^{15}$ ions cm$^{-2}$s$^{-1}$

Ion Dose

The ion dose, $D_i$, for 1 h treatment, $t = 3600$ sec is given by

$D_i = N_i \times t = 6.25X10^{15} \times 3600 = 2.25x10^{19}$ ions cm$^{-2}$
Neutral Dose

Since the neutral flux is a factor of $L/\lambda$ of the ion flux, the neutral dose, $D_n$ is given as

$$D_n = D_i \times L/\lambda = 2.25 \times 10^{19} \times 1.49 = 3.3 \times 10^{19} \text{ neut cm}^{-2}$$

Number of Sputtered Silicon atoms, $N_{sp}$

Assuming an average angle of incidence of $35^\circ$,

The Sputtering Yield by Ions, $Y_s^i = 0.398 \text{ atoms ion}^{-1}$ and

The Sputtering Yield by Neutrals, $Y_s^n = 0.180 \text{ atoms neutral}^{-1}$.

Then for a unit area (1 cm$^2$) the number of sputtered atoms, $N_{sp}$ is given as

$$N_{sp} = (\text{Ion Dose} \times Y_s^i) + (\text{Neutral Dose} \times Y_s^n)$$

$$= (2.25 \times 10^{19} \times 0.398) + (3.3 \times 10^{19} \times 0.18)$$

$$= 1.49 \times 10^{19} \text{ atoms}$$

Depth of Sputtered Area

Atomic density of silicon = $4.96 \times 10^{22} \text{ atoms cm}^{-3}$.

The volume of sputtered material $V = d \times A$

where $d =$ depth of sputtering and $A =$ area sputtered

However, the volume of sputtered material = Volume of atoms sputtered, hence for a unit area of sputtered material,

$$\text{depth, } d = \frac{1.49 \times 10^{19} \text{ atoms}}{4.96 \times 10^{22} \text{ atoms cm}^{-3}} = 2.98 \mu\text{m}.$$
Appendix 3

Sample Calculation of Experimental Sputtering Yield

The sputtering yield from experimental results assumes that the number of atoms removed occupies the volume of material sputtered. The depth of sputtering, $d$, is measured by profilometry.

Let $\rho =$ Atomic density of substrate $\quad N_{sp} =$ # of sputtered atoms
$V =$ Volume occupied by atoms $\quad A =$ Area of sputtered atoms and
$d =$ Depth of sputtering.

Then

$$N_{sp} = V \times \rho \quad = A \times d \times \rho$$

For a depth of 4.3 $\mu m$ of unit surface area on silicon

$$N_{sp} = 4.3 \times 10^{-4} \times 1 \times 4.96 \times 10^{22} = 2.1 \times 10^{19} \text{ atoms}$$

If

$$N_i =$ # of ions $\quad N_n =$ # of neutrals $\quad N_p =$ Total # of particles
$t =$ Time (sec) and $\quad Y_s =$ Sputtering Yield

Then

For $N_i = 1 \times 10^{16}$ ions $\quad N_n = 1 \times 10^{17}$ neutrals $\quad t = 3 \text{ h}$

$$N_p = (N_i + N_n) \times t \times A = (1 \times 10^{16} + 1 \times 10^{17}) \times 3 \times 3600 = 1.19 \times 10^{21} \text{ particles}$$

$\Rightarrow$ Sputtering yield, $Y_s = \frac{N_{sp}}{N_p} = 0.018 \text{ atoms particle}^{-1}$
Appendix 4

Sample Calculation for Determining Nitrogen Concentration from AES Data

Auger results are data for the determination of elemental composition in the near-surface region. Quantitative analysis by AES is made by measuring peak-to-peak height differences at identified electron energies and applying relative sensitivity factors. Nitrogen content estimation in TiN is complicated by the fact that the main Auger emission from nitrogen occurs at an energy level that completely overlaps the L3M2,M3 transition from titanium at 378-385 eV. The combined peak-to-peak height of nitrogen and titanium is measured at 378-385 and the nitrogen contribution to the peak can be estimated by subtracting the titanium contribution. The titanium contribution on the other hand can be derived from the peak height of the clear Ti (420 eV) transition.

Assuming the combined Ti+N peak at 385 eV is represented as \( P_{(385)}^x \) for a sample with a N to Ti atomic ratio of \( x \) we have:

\[
P_{(385)}^x = P_{N(385)}^x + P_{Ti(385)}^x \quad (1)
\]

If it is also assumed that the relative nitrogen and titanium sensitivity ratio \( S_{N(385)}/S_{Ti(420)} = S_{rel} = 1.92 \) and is independent of nitrogen concentration, then

\[
k_{Ti} = \frac{P_{Ti(385)}^x}{P_{Ti(420)}^x} = \frac{P_{N(385)}^x}{P_{Ti(385)}^x} = 0.69 \quad (2)
\]

Thus the nitrogen contribution to the 385 eV peak can be calculated by:

\[
P_{N(385)}^x = P_{(385)}^x - k_{Ti} P_{Ti(420)}^x \quad (3)
\]

The atomic ratio \( x \), of N to Ti can be written as

\[
x = \frac{P_{N(385)}^x}{P_{Ti(420)}^x} (S_{rel})^{-1} \quad (4)
\]

186
Alternatively, writing the above expression in terms of observable peak height ratio, $R_x$
defined by

$$R_x = \frac{P_{x(385)}}{P_{x(Ti(420))}}$$

is producing

$$x = \frac{(R_x - k_T)}{S_{ref}}$$

All titanium and nitrogen composition calculations in the present work were based on the aforementioned method.
Appendix 5

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Albert A. Adjaottor
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USA

Lausanne, 19 November 1996

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VITA

Albert Amatey Adjaottor was born to a Senior Labor Officer and a Nursing Sister on January 31, 1960 at Koforidua in the Eastern Region of Ghana. After a series of cross-country settlements with his father he settled in Accra and had his elementary education at Cambridge Preparatory School. After seven years of elementary education he gained admission to the prestigious Achimota Secondary School in Accra, Ghana, formerly known as the Prince of Wales College. He graduated with distinction in June 1978 on the GCE Ordinary-Level examination and regained admission to Achimota School for a two-year pre-university course in mathematics, physics and chemistry.

After a gruesome two years, his success at the GCE Advanced-Level earned him admission to the University of Science and Technology (UST) in Kumasi Ghana amid keen competition. He studied Chemical Engineering with hopes of working in the petroleum industry. Upon graduation with honors with a Bachelor of Science in Chemical Engineering, he served as a Teaching Assistant in the department at UST. He later gained admission to Louisiana State University (LSU), and on starting his studies at LSU experienced a change in interest to that of the study of materials. He gained a Master of Science in Chemical Engineering in May 1992 and continued to pursue a Doctor of Philosophy program under the inter-disciplinary Engineering Science Program. He was admitted into the Materials Science and Engineering Program of the Mechanical Engineering Department (LSU). He is currently a candidate for the degree of Doctor of Philosophy in Engineering Science to be awarded at the Fall commencement, 1997.
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Albert Amatey Adjaottor

Major Field: Engineering Science

Title of Dissertation: A Study of the Effect of Energetic Flux Bombardment on Intensified Plasma-Assisted Processing

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination: 9/10/97

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