CHAPTER 1
INTRODUCTION

1.1 Titanium

The first discovery of titanium as an element was by Reverend William Gregor in 1791. He recognized the presence of a new element, now known as titanium, in menachite, a mineral name after Menaccan in Cornwall, England. Several years later, the element was rediscovered in the ore rutile by a German scientist, Klaproth. Titanium, in pure elemental form was first made by Matthew A. Hunter, who heated titanium tetrachloride (TiCl₄) together with sodium in a steel furnace at 700-800°C [1]. But, only in the last 40 years or so; titanium has gained strategic importance [2]. Titanium is the fourth abundant structural metal, after aluminum, iron and magnesium. Many methods to isolated titanium from its ore were attempted. In 1930, Dr. Wilhelm J. Kroll has developed a relatively safe and economical method to isolate titanium from its ore, and this was to be the catalyst for remarkable growth in titanium consumption [2]. Kroll's process involved the reduction of TiCl₄ with sodium and calcium, and later with magnesium in inert atmosphere. The first commercial mill product produced by magnesium reduction was by Titanium Metals Company of America in 1950 [3].

Titanium and titanium alloys possess several excellent properties including good corrosion resistance and high strength to weight ratio. It is lightweight and the ability
to withstand extreme temperatures makes it suitable for aerospace applications [4]. Titanium is a low-density element (about 60% of density of steel), and can be strengthened by alloying and deformation processing. Titanium is also non-magnetic, has a lower thermal expansion compared to steels and less than half compared to aluminum. Its melting point is 1670°C, higher than that of steel [5]. Titanium, when exposed to oxygen containing environment readily form a stable, protective oxide layer, thus rendering its excellent corrosion resistance properties [2]. Table 1.1 below lists some applications of titanium and its alloy in industry [6].

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<tr>
<td>1.</td>
<td>Aerospace</td>
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<td>2.</td>
<td>Medical (implants)</td>
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<td>3.</td>
<td>Automotive</td>
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<td>4.</td>
<td>Gas turbine engines</td>
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Table 1.1: Applications of titanium and titanium alloys.

For application subjected to sliding or friction, titanium and its alloys do not offer adequate wear resistance. To improve on this, treatment such as coating, nitriding and oxidizing is needed [8]. The most popular way to improve the corrosion and wear property of titanium is by forming or applying a thin layer of titanium nitride (TiN) on the surface of titanium. This is because titanium nitride has many desirable
properties for wear and corrosion resistant application. These properties are summarized in Table 1.2:

<table>
<thead>
<tr>
<th>Appearance</th>
<th>Yellow-brown</th>
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<tbody>
<tr>
<td>Density</td>
<td>5430 kg/m³</td>
</tr>
<tr>
<td>Hardness</td>
<td>TiN has a hardness value of 2160 kg/mm² (30g) in knoop or Vickers number. This makes TiN a material of choice in wear application, such as cutting tools.</td>
</tr>
<tr>
<td>Friction of coefficient</td>
<td>Compared to pure titanium, TiN provides relatively low friction properties.</td>
</tr>
<tr>
<td>Corrosion/Chemical resistance</td>
<td>Highly resistant to most acids, bases, solvents, etc.</td>
</tr>
<tr>
<td>Temperature Resistance</td>
<td>Oxidizes at 600° C in air</td>
</tr>
<tr>
<td>Melting Points</td>
<td>3290° C</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>28.84 W/m/K at 25° C</td>
</tr>
<tr>
<td></td>
<td>16.72 W/m/K at 200° C</td>
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<tr>
<td></td>
<td>8.36 W/m/K at 1000° C</td>
</tr>
<tr>
<td></td>
<td>67.72 W/m/K at 1500° C</td>
</tr>
<tr>
<td>Toxicity</td>
<td>Non-toxic, approved by FDA for surgical tools and implants</td>
</tr>
</tbody>
</table>

Table 1.2: Properties of titanium nitride.
1.2 Surface treatment technologies of titanium

Coating technology for applying TiN mainly evolves around techniques called physical vapor deposition (PVD) [9,10,11] and chemical vapor deposition (CVD) [12,13]. In PVD techniques, solid materials need to be vaporized or atomized to transport them to the substrate, by heat or by an energetic beam of electrons, photons (laser ablation) or positive ions (sputtering) [14]. Through PVD method, titanium is evaporated in nitrogen containing environment to formed titanium nitride. Meanwhile, CVD refers to techniques of film deposition using gases, evaporating liquid or chemically gasified liquid as source materials [14]. To deposit TiN by CVD method, TiCl₄ is employed as a precursor, with ammonia or nitrogen as oxidants. Both PVD and CVD are coating techniques, whereby another layer is deposited on the substrate surface. Diffusion technique, such as nitriding is used to form nitride layer on the surface of titanium.

1.3 Titanium-nitrogen phase diagram

Titanium nitride may exist in various forms, as shown in the Ti-N phase diagram in Figure 1.1. The equilibrium solid phases of Ti-N system shown are: (1) the closely packed hexagonal (cph) solid solution, (alpha Ti), for Ti below 882°C, (2) the body centered cubic (bcc) solid solution (beta Ti) when Ti is heated to above 882°C, (3) the tetragonal Ti₂N(β) phase, ε, with small composition range at 33.3 % N, (4) the face centered cubic (fcc) TiN phase, δ and (5) the body centered tetragonal (bct), Ti₂N(α), δ', with small range of composition near 37.5 % N.
1.4 Plasma sources for materials processing

Plasma technology is widely employed to modify the surface properties of materials. Thin film deposition, either by physical vapor deposition (PVD) or chemical vapor deposition (CVD), uses plasma to enhance or modify the properties of the resulting materials. For surface modification processes, such as nitriding, etching and ion implantation, the use of plasma is indispensable. It is not surprising that plasma technology has become essential in modern manufacturing technology. To illustrate the importance of plasma technology for the next millennium, a report by National Academy of Science [15] stated that:
"Plasma processing technologies are of vital importance to several of the largest manufacturing industries in the world. Foremost among these industries is the electronic industry, in which plasma-based processes are indispensable for the manufacture of very large scale integrated (VLSI) microelectronics circuit (or chips). Plasma processing of materials is also a critical technology in, for example, the automobile, steel, biomedical and the toxic waste management industries. Most recently, plasma processing technology has been utilized increasingly in the emerging technology of diamond film and superconducting film growth. Because plasma processing is an integral part of so many vital American industries, it is important for both the economy and the national security that America must maintain a strong leadership role in this technology."

Many plasma sources have been developed for the application in materials processing areas, such as Radio Frequency (RF), microwaves and DC plasma sources. This report will concentrate on the development and application of an RF inductively coupled plasma source.

1.4.1 RF discharges

Radio Frequency (RF) driven discharge can be divided into two categories; 1) capacitive discharge and 2) inductive discharge. Capacitive driven discharge, or sometimes called RF diodes, is the most common source for materials processing [16]. The RF capacitive discharge system consists of two separate electrodes driven
by an RF power source in a controlled chamber. The configuration of a basic system is shown in Figure 1.2.

![Figure 1.2: A symmetrical RF discharge system.](image)

The capacitor of low RF impedance is placed in series with the electrodes. A high voltage is applied across the electrodes, which leads to the formation of plasma. Another variation to capacitively driven discharge is an asymmetric configuration, as shown in Figure 1.3.

![Figure 1.3: An asymmetrical RF discharge system.](image)
In this case one electrode is the grounded chamber, making the relative areas of the electrodes very different. Usually, the smaller electrode is powered. In the plasma, the electrons are relatively free to respond to the applied high voltage. The ions are too massive to respond at frequency above 100 KHz. Therefore, as the electrode is powered more positive relative to the ground, it will rapidly collect electrons, while the other electrode will collect ions, but at a much slower rate. A steady state is reached when the time average electron current balances the ion current. At this point the powered electrode will maintain at negative bias of approximately half the applied peak-to-peak RF voltage as shown in Figure 1.4. This type of configuration is commonly used in RF sputtering for thin film deposition. Plasma density, $n$, produced by RF capacitive discharge is typically of the order of $10^{10}$ to $10^{11}$ cm$^{-3}$ [17].

![Diagram of voltage and time relationship in RF discharge system.](image)

Figure 1.4: The potential of the powered electrode for assymetrical system.

### 1.4.2 Inductive discharge

A limiting feature of RF diodes is that the ion bombarding flux and the ion acceleration energy cannot be varied independently. Furthermore, since the electrodes
are present in the processing chamber, impurities originating from these electrodes are unavoidable. This has led to the development of new generation of new high efficiency power source. One of such power source is RF inductively Coupled Plasma (ICP) source.

Inductive discharge was first reported by Hittorf in 1884. In 1970, open-air induction torch was developed for use in mass spectroscopy. In 1990, an inductively coupled plasma source was patented by Ogle [18] and by Coultas and Keller [19]. Since then, much works had been done on the theoretical and experimental aspect of the ICP source, such as Hopwood et al [20], Meyer et al [21] and El-Fayoumi et al [22,23]. Nowadays, inductive discharge has found many applications in material processing and manufacturing industries, such as etching and thin film deposition.

The inductive discharge is produced by application of an RF power to an inductive coil. The ICP is created by an RF current passing through a coil that generates an RF magnetic field. This magnetic field induces a circular electric field whose lines of force are concentric with the primary coil current. Plasma density created by inductive discharge is typically a factor of 10 times higher than the capacitive discharge plasma, in the range of $10^{11}$ to $10^{12}$ cm$^{-3}$[16]. There are many inductive source configurations, such as planar, helical and antenna. However, our scope will be limited to inductive discharge produced by planar coil configuration.
1.4.3 Planar coil inductively coupled plasma

The planar coil inductively coupled plasma was developed in the 1980's, and since then there have been much interest in the use of high-density induction discharge for material processing at low pressure. The planar coil configuration is a flat spiral coil placed outside the process chamber with a dielectric window (such as quartz plate) separating the coil and the process chamber. In an inductive discharge, the induction coil does not require to be part of the plasma, thus enabling the substrate to be manipulated. For example, the substrate may be biased at negative voltage to enhance ion bombardment onto the substrate.

A planar coil generates an inductive field consisting of three components, \( H_r(r,z) \) and \( H_z(r,z) \), and also an electric field \( E_0(r,z) \). With the absence of plasma, the RF magnetic field lines encircling the coil are symmetrical with respect to the plane of the coil, as shown in Figure 1.5(a). With the presence of plasma, according to Faraday's law, an azimuthal electric field, \( E_0 \) and associated current density \( J_0 \), is induced within the plasma. The current component \( J_0 \), in opposite direction to the coil current, is confined to a layer near to the surface having thickness of the order of skin depth \( \delta \). The total magnetic field is then the sum of the magnetic field produced by the coil current and the single turn induced plasma current, as shown in Figure 1.5(b). The dominant magnetic field components within the plasma are \( H_z \) near the axis, and \( H_r \) away from the axis [24].
Figure 1.5: Schematic diagram of RF magnetic field near a planar coil (a) without plasma (b) with plasma [24].
1.5 Nitriding

Nitriding is a process in which nitrogen is diffused into the surface of materials in contact with nitrogen atmosphere. The history of nitriding began in 1900, when Dr. Adolph Fry discovered that nitrogen and iron had an affinity to form nitride when in contact under heat. If heat is applied to iron and nitrogen gas, nitrogen will diffuse into the surface of iron, creating a structural change in its surface and increasing its hardness. Following that, there have been many development works on the practical application and cost of nitriding are being carried out in industry [25].

Nitriding can be achieved by different methods, such as gas nitriding, liquid nitriding and plasma (ion) nitriding. In the gas nitriding method, a material is heated to a certain temperature (495-565° C in case of steels), holding it at that temperature for specified duration, in nitrogen containing atmosphere in a furnace. For liquid nitriding or also known as salt bath nitriding, the hardening medium is a molten, nitrogen bearing, fused salt bath containing either cyanides or cyanates, at temperature 510-580° C. Another method of nitriding, ion nitriding or also known as plasma nitriding, utilizes glow discharge to introduce elemental nitrogen to the material surface for subsequent diffusion into the material [26].

1.5.1 Plasma Assisted Nitriding Techniques

The early work in the field of plasma nitriding started in 1930. The jumpstart of this technology was the desire to be able to shorten cycle time, reduce distortion and improve upon the metallurgical problem and properties associated with conventional
(gas and liquid) nitriding [25]. The earliest concept of plasma nitriding is based on DC diode configuration. A high voltage (typically in the range of 300-2000V) is applied between the anode (grounded chamber) and the cathode (substrate), as shown in Figure 1.6.

![Schematic diagram of DC nitriding system.](image)

In DC diode arrangement, the substrate is connected to the cathode (negative electrode). A high voltage is applied between the cathode and a grounded chamber, creating a glow discharge. The energetic positive ions bombard the substrate, thus heating up the substrate. At sufficiently high temperature, usually above alpha/beta transformation temperature nitriding process can take place [27]. DC diodes nitriding is relatively slow and this has led to the development of an enhanced plasma assisted nitriding concept [28].

Several types of enhanced plasma nitriding techniques include: 1. thermionically assisted DC triode (TAT) [29-36]. 2. plasma immersion ion implantation (PIII)
3. electron cyclotron resonance (ECR) [39,40]. thermionic arc discharge (TAD) [41,42]. 5. inductively coupled plasma (ICP) [43,44].

In this project, an inductively coupled plasma technique is used for nitriding of titanium.

1.6 Objective and thesis organization

The objective of this work is to demonstrate the ability of a planar coil inductively coupled plasma source for nitriding of titanium metal. The organization of the thesis is as follows: Chapter 2 describes the set up and various components of the system, and techniques and methods that have been used for plasma diagnostics and sample characterization. Chapter 3 describes the discharge characteristics of the system. In chapter 4 the application and the usefulness of the system for nitriding of titanium is discussed. In chapter 5 the conclusion and suggestions for future works is presented.