I, Jin Woo Seok, hereby submit this as part of the requirements for the degree of:

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Sputter Deposited Cr/CrN Nanocrystalline Thin Films

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ABSTRACT

Nano-crystalline Cr/CrN coatings have been deposited on 1010 steels and Si (100) wafers using a pulsed DC magnetron sputter deposition technique. Effects of the nitrogen content in the sputtering gas on properties of as deposited and IR heat treated coatings were investigated in detail. With increasing nitrogen contents in the sputtering gas, microhardness and adhesion strength of coatings increases. The hardness of coated steel was twice as high as the steel substrate alone when the nitrogen content in the sputtering gas is 7% and a load of 25 g was applied. Critical loads of deposited coatings increase from 0.16 kg with 0% N₂ to 2.07 kg with 7% N₂ in the gas. From stability analysis of Cr, CrN, and Cr₂N phases, the Cr-N binary phase diagram was modified to include an eutectoid reaction at 430°C.

The infrared (IR) heat treatment was found to increase the bonding strength of coatings on steels. Analysis showed that the microstructure and hardness of coated steels were not changed due to the IR heat treatment. However, the adhesion strength measured using a scratch test was improved from the IR heat treatment. The critical load of film debonding of coatings deposited with 5% N₂ increases from 0.92 to 1.38 kg by the IR heat treatment. The results suggest that the scratch test can be a sensitive technique to detect minor modifications in the property of the coating.
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The author expresses his gratitude to his fellow students, Jr-Hung Li, Haichuan Mu, Yimin Wang, Kumar Chokalingam, and Pranav Deshpande. The author thanks Dr. Eun T. Park and Euisuk Park for their invaluable discussions throughout this research. The author would like to give thanks to Douglas Bowling, Dale Weber, Joseph Williams, Beth Walker and Charlotte Poole for their help with this project.

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1. INTRODUCTION

Coatings impart to engineering components with properties such as improved wear resistance, good corrosion resistance, low friction coefficients and attractive appearances. Coating with thin chromium layers has been important engineering practices for years in automotive, aerospace and decorative industries for various reasons. They are used as wear and/or corrosion resistant coatings, coatings for bright and non-tarnishing surfaces, and high temperature coatings. Depending on the applications, chromium coatings are often classified into the following categories:

(1) “Thin” decorative coatings (thickness < 0.5 \( \mu \text{m} \)): These coatings offer good corrosion resistance and non-tarnish surface. The structure is usually crack-free and nonporous. These are used in automobile trims.

(2) “Hard chrome” coatings (thickness > 2.5 \( \mu \text{m} \)): These coatings offer high hardness (>1000 VHN), wear resistance, low coefficient of friction etc. Conventional “hard chrome” coatings produced by electrochemical process generally have cracks normal to the face and extending through the thickness. Therefore they don’t have good corrosion resistance. These cracks are believed to have resulted from the deposition of a large quantity of chromium (Cr) hydrides formed during processing [1]. Chromium hydride subsequently decomposes to chromium and hydrogen at ambient temperature with 15 vol.% shrinkage. Since one side of the coating is constrained by the base metal, cracks in coatings develop normal to the surface. Hard chromium coatings are used in coating tools, dies, fittings, or babbitts.
(3) Microcracked coatings (> 0.75 µm): These coatings have good corrosion resistance, fatigue properties (low notch sensitivity) but are softer than conventional “hard chrome” coatings [2],[3]. They are used for oxidation resistance. They also appear as “duplex Cr” coatings in which the first layer is a thin crack-free coating and the second layer is a much thicker microcracked coating. The corrosion resistance of the “duplex Cr” coatings is superior to the regular thin or hard Cr coatings because of the many small electrochemical cells resulting from such a configuration [4]. The bath composition, particularly SO$_4^{2-}$ concentration, has a strong influence on the microcrack density. The current density, deposition efficiency and temperature of bath also influence the microcrack density [3].

(4) Porous coatings: These coatings are utilized because of their oil retention capabilities. The porosity is obtained by treating the chromium coating in an etching solution [5].

Other kinds of Cr coatings include Low-concentration (LC) coatings [6] and implanted coatings [7]. The LC coatings have high tensile strength and microhardness, and are reported to be produced by pulsed DC plating [6],[7]. This process allows for removal of the concentration gradient in the electrolyte between the pulses and hence increases deposition rate. N$_2$ implanted coatings are used for their better wear resistance [7].

The conventional way of producing these coatings is by electrodeposition. The annual production of Cr coated steels is estimated to be in the order of billion tons of coatings are produced and electroplating of chromium is multi-billion tons which results
in a multi billion dollar business for electroplating of chromium nationwide [8],[9]. However, during electrodeposition, carcinogenic vapors of hexavalent chromium (Cr\textsuperscript{6+}) are released from the CrO\textsubscript{3} used in the bath. The U.S. environment protection agency (EPA) has recently imposed very stringent requirements on the emission control for such industries. Table I and II show the proposed new limits for chromium electroplating industries and the requirements for hard chromium coatings in automotive industry. The approximate cost for the industries to operate under such enforcement is predicted to be hundreds of million dollars [9]. Hence, alternate methods are being developed to deposit these coatings in an economic yet environmentally safe process. Sputter deposition has essentially no Cr\textsuperscript{6+} emission since it involves transfer of vapor atoms instead of ions. Hence, the sputter deposition is a strong candidate to produce low cost chromium coatings. However, the hardness of sputter deposited pure chromium coatings are not as high as electrodeposited coatings, where the hardness is believed to have derived from presence of complex hydrides. This problem can be solved by incorporating nitrogen in the sputtering environment in a process known as reactive sputter deposition [9],[10]. Depending on the nitrogen content, the coating consists of either chromium phase with nitrogen dissolved in the lattice or the chromium nitride (CrN) phases. Either way the hardness of these coatings goes up.

**Statement of Objective and Scope of Work**

One of the objectives of the thesis was to investigate effects of the nitrogen concentration on sputter deposited hard chromium coatings for wear resistant applications. The wear resistance, microhardness, and adhesion of the coatings deposited
by reactive sputter deposition are sensitive to numerous parameters involved such as temperature of deposition, nitrogen content, sputter power etc. Some properties are sensitive to a combination of these parameters.

The second objective of this thesis was to investigate the infrared (IR) heat treatment on the adhesion property of Cr/CrN coatings on steels. Adhesion properties of the coating layer are critical in the application of wear resistance coatings. Direct contact between Cr/CrN coating layers and steel substrates generates relatively high thermal stress at its interface and causes poor adhesion since coefficients of thermal expansion of chromium and steel are $6 \times 10^{-6}/^\circ\text{C}$ and $11 \sim 15 \times 10^{-6}/^\circ\text{C}$, respectively.
Table I  EPA proposed new limits for electroplating emission.

(a) Small means tanks having a maximum potential rectifier capacity of less than 60 million ampere-hours per year. Existing means installed before 12/16/93.

(b) Includes new tanks.

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<td>Small, existing tanks</td>
<td>0.03 mg/dscm</td>
<td>Packed-bed scrubber (PBS)</td>
</tr>
<tr>
<td>All other tanks (b)</td>
<td>0.015 mg/dscm</td>
<td>Composite mesh-pad (CMP) system</td>
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<td>All tanks (b)</td>
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<th>Strut 2.5 cm dia. × 46 cm length</th>
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<td>Plating Thickness</td>
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<td>45 mm</td>
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<td>Minimum of R&lt;sub&gt;C&lt;/sub&gt; 82</td>
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<td>After 48 hours of salt spray, an average of 3 sites per rod in test group or 10 sites maximum on one rod</td>
<td>After 48 hours of salt spray, an average of 3 sites per rod in test group or 10 sites maximum on one rod</td>
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2. BACKGROUND

2.1 Hard Cr Coatings

In the automotive industry 1040 steel rods used in shocks and struts are coated with Cr to increase their durability. Traditionally the coatings have been applied by means of electrodeposition. The Chromium coatings also are used to improve the corrosion resistance of the shocks and struts.

Most of chromium coatings used in the industry are produced using electrochemical processes. The bath usually contains chromic acid (CrO₃), water, and catalysts (sulfate and/or fluoride radicals in the form of sulfuric acid, sodium sulfate, fluorosilicic acid or silicofluorides). The use of hexavalent Cr usually results in hazardous by-products [9]. Some research groups have tried to use trivalent Cr solutions for chromium coatings [10],[11]. The quality of Cr coatings produced from trivalent chromium solutions is not good enough in terms of their appearance. Bright surface finishes are very difficult to obtain. Deposition rates with trivalent Cr are lower than those using hexavalent chromium solutions.

Chromium films are used in many applications including wear and corrosion resistance and electronic applications. Chromium coatings produced by sputter deposition can have mirror like appearance and provide good oxidation resistance to the base metal. Chromium coatings and films produced by using sputter deposition have been studied in various systems [10]~[18]. Sputter deposited chromium films have been characterized for the structure and morphology by different workers on various substrates such as steel, glass, silicon, single crystal rock salt, and aluminum. As mentioned above, sputter deposited pure Cr coatings show relatively low hardness compared to
electrodeposited Cr coatings. The Cr films, which were deposited at 200°C using RF sputter deposition, were found to have strong \{110\} preferred orientation [13]~[15]. The preferred orientation of the deposited films changes to \{100\} with increasing the substrate temperature. Cr films deposited at 200°C shows that Cr and CrN phases when the nitrogen gas exists in the sputtering gas. Straight columnar structures with dome tops are found extending outwards from the substrate surface. The width of these columns increases with increasing thickness of the films. The Cr films deposited at 400°C shows Cr and Cr$_2$N phases when the nitrogen gas exists in the sputtering gas. Hardness of Cr films deposited decreases with increasing the substrate temperature due to the thermal stress.

2.2 Physical Vapor Deposition (PVD)

Sputtering is a process whereby material is ejected from the surface of a solid or a liquid due to the momentum exchange associated with surface bombardment by energetic particles [19]. Sputter deposition is a vacuum coating process. A source of coating materials, the target, is placed in a vacuum chamber along with the substrates, and the chamber is evacuated to a pressure in a range $10^{-4}$ to $10^{-7}$ Torr. The bombarding species are generally ions of heavy inert gas. Argon is the most common gas used as bombarding species.

The most common method of providing the ion bombardment is to backfill the evacuated chamber with the inert gas to a pressure of from 133.3 to 13.33 Pa (1 to 100 mTorr) and ignites an electric discharge so that ionization of the working gas is produced in the region adjacent to the target. Such a low-pressure electric discharge is called a
A glow discharge is defined as a partially ionized gas containing equal volume concentrations of positive and negative charged species (ions and electrons) and different concentrations of neutral and exited species [20]. The partially ionized gas can be produced either by subjecting the gas to very high temperatures (e.g. by laser heating, electron beam heating, or by using shock waves) or by subjecting the gas to strong electric or magnetic fields. Plasma can be classified into “thermal” plasma, where ion, electrons and neutrals are in local thermodynamic equilibrium (LTE), and the temperature of electrons is equal to that of the heavy particles, or “cold” or non-equilibrium plasmas, where electrons and ions are more energetic than the neutral species. Cold plasmas are typically used in sputtering processes.

2.2.1 Formation of a glow discharge

The voltage distribution across a dc glow discharge region in a low-pressure gas, using a high impedance power supply, is shown in Fig. 2.1 [21]. On application of a small voltage, a very small current flows due to the small number of initial charge carriers in the system (the inert gas contains a negligibly small number of ions generated by the background cosmic radiation). As the voltage increases, the current remains constant since the moving charge carriers do not have sufficient energy to ionize the neutral gas atoms or the solid electrode atoms. Beyond a certain voltage, the charged particles acquire sufficient energy to create more charge carriers by two processes – ionization of neutral gas atoms and ion collisions with the cathode resulting in the
Fig. 2.1  Voltage distribution across a dc glow discharge [21].
formation of secondary electrons. At this stage, the current starts to rise rapidly, although the voltage remains constant, since it is constrained by the output impedance of the power supply. This region of constant voltage and increasing current is called the Townsend discharge.

Beyond a certain current density, a large number of electrons and ions are created through repetition of the above processes, and the discharge becomes self-sustaining when the numbers of fresh electrons generated produce enough ions to regenerate the initial number of electrons. At this point, the voltage decreases while the current increases. The present glow discharge maintains itself at a constant voltage. This state of the discharge is referred to as the “normal” glow. During the early stages of the normal glow, the cathode surface is only partially covered by the glow, since ion bombardment of the cathode is concentrated at the edges and at surface irregularities. With increased power, the glow covers the entire cathode. This state of the discharge is called the “abnormal” discharge that is the regime in which sputtering processes are performed. Further increase in power, results in the formation of arcs (i.e. the voltage drops to low levels as current rises rapidly).

A basic requirement for forming an abnormal discharge is to achieve the “breakdown” voltage, $V_p$, as shown in Fig. 2.1. This voltage has been established to depend on two parameters, the distance between cathode and anode and the mean free path of secondary electrons. The relationship between the breakdown voltage, the electrode separation distance, the gas pressure, which determined the electron mean free path, is given by Paschen’s law [22].

$$V_p = a \left( \frac{Pd}{\log(Pd) + b} \right)$$  \hspace{1cm} (2-1)
where \( a \) and \( b \) are constants, \( P \) is the gas pressure, and \( d \) is the electrode separation distance. Paschen’s law is graphically shown in Fig. 2.2. The minimum breakdown voltage is called the Paschen minimum. This law indicates that if the separation distance of the electrodes and/or the pressure is too large, ions in the plasma loose energy through inelastic collisions and do not have sufficient energy to create secondary electrons at the cathode. An important application of Paschen’s law is the design of the minimum separation distance between the target and dark space shields (or ground shields). The basic design criteria is that \( V_M \), the maximum discharge voltage, should be less than \( V_P \), the value of the breakdown potential corresponding to a separation distance, \( d \) [22].

Collision process in the plasma are typically characterized by a collision cross section, \( \sigma \), which has the dimensions of area. If collisions occur between an electron and neutral species, then the mean free path, \( \lambda \), for the collision process is defined by

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

(2-2)

where \( N \) is the density of the neutral species per unit volume and \( \sigma \) is the collision cross section. Another important parameter in collision process is the collision frequency, \( \nu \), which is defined by

\[
\nu = N\sigma\nu = \frac{\nu}{\lambda}
\]  

(2-3)
Fig. 2.2 Paschen’s curve showing that the voltage required to sustain a plasma as a function of the product of the electrode spacing and gas pressure [22].
where \( v \) is the electron velocity.

The properties of the glow discharge are determined by collisions between electrons and all other species within the plasma. The collisions can be either elastic (internal energy of the colliding species is conserved) or inelastic collisions (internal energy is not conserved). The main categories of elastic collisions in the plasma include electrons-neutral collisions and electron-electron collisions. However, inelastic collisions tend to be the dominant collision process in the glow discharge.

One of the important inelastic collision processes to maintain the discharge is electron impact ionization. A typical reaction is expressed by

\[
e^{-} + Ar \rightarrow Ar^{+} + 2e^{-} \quad (2-4)
\]

The two electrons can ionize more Ar and the discharge can be sustained.

The target is negatively biased in order to be bombarded by positive ions. The most direct method for providing the plasma and allowing the target to be bombarded by ions is simply to make the target the cathode, or negative electrode, of the electric discharge. Applied potentials between the target and the anode are typically from 500 to 5000 V. A sputtering apparatus with this design is called a diode. Fig. 2.3 shows a schematic diagram of a planar diode sputtering source.

In the glow discharge, neutral atoms, positively charged ions, and electrons exist. The electrons are accelerated toward the anode by the electric field and produced additional ions. The ions are accelerated toward the cathode and produce secondary
Fig. 2.3  Schematic diagram of a planar diode sputtering source.
electrons. By the impact of positive ions on the cathode surface, the atoms of the cathode material will be ejected. These ejected atoms travel across the space and condense on the substrate to form the film. The particles sputtered from the target, cathode, are neutral and their average energy is considerably higher (5~20 eV) than that of thermally evaporated atoms.

2.2.2 Sputter deposition process

The biggest advantage of sputter deposition is that any material can be produced in the form of films. Since the coating material is sputtered into the vapor phase by physical processes rather than thermal or chemical processes, virtually any material is a candidate for coating. Sputter deposition processes can be classified into four categories - direct current (DC), radio frequency (RF), magnetron and reactive sputtering.

DC sputtering

The simplest configuration for sputter deposition is the dc diode sputtering system as shown in Fig. 2.4 (a). The target, which is mounted on the anode, is connected to the negative voltage supply while the substrate is facing the target. The primary requirements for the power supply is determined by the size of the target and typically should be capable of providing up to 10 W cm\(^{-2}\) at voltage between 1 to 5 kV. The actual power applied is calculated by the applied voltage, gas pressure, type of gas, and the secondary electron yield from the target surface [21]. An important feature required in the power supply is the ability to distinguish between catastrophic arcing (metal flakes cause a short circuit between the target and ground) and minor arcing (when insulating
Fig. 2.4 Schematics of simplified sputtering systems (a) DC and (b) RF [21].
components are present on the target surface, local dielectric breakdown happens). Catastrophic arcing causes automatic shut down of the power supply. The glow discharge is started by introducing an inert gas at pressure of 1.33 to 13.3 Pa (5 to 100 mTorr). Once the glow discharge is started, the sputter deposition process begins and target atoms begin to condense on the substrate. The collision of target atoms with gas in the plasma causes scattering and target atoms tend to arrive at the substrate with random directions and energies. Consequently, increasing the distance between the target and the substrate increases the possibility of sputtered material being lost to the chamber walls, etc.

The deposition rate in DC diode sputtering processes is strongly influenced by the sputtering pressure and the discharge current. At low pressure, the ionization efficiency is low (ignition of the glow discharge requires a pressure of at least 1.33 Pa (10 mTorr) and consequently very low deposition rates are obtained. As the voltage increases, the electron energy increases, the mean free path decreases, the ionization efficiency is low, and therefore the discharge current is limited. Meanwhile, the electron mean free path increases with decreasing pressure increasing the sputtering pressure, results in a decreased mean free path, enhanced impact collisions in the discharge (the ionization degree increases), and consequently the deposition rate increases. Beyond a certain level, however, the increased ionization of the sputtering gas is offset by the decreased mean free path of the sputtered atoms.
RF sputtering

RF sputtering was developed to deposit insulating films (with resistivities above $10^7 \, \Omega \, \text{cm}$). The concept of sputtering insulating materials using a capacitively coupled high frequency discharge was initially reported by Wehner [23]. Later Davidse provided practical demonstrations of the principle using a frequency of 13.56 MHz. RF technologies have been developed and reviewed by Vossen [24], Champman [20], and Jackson [25].

The main principle of depositing insulating films using RF sputtering is applying a rapidly varying ac voltage to an insulating target (Fig. 2.4 (b)). Since there is no dc path through the electrode, the average flow of ions and electrons to the target surface during each cycle must be the same to preserved charge neutrality. The highly mobile electrons provide sufficient charge during a small fraction of the cycle time to neutralize the positive ion charge that flows during the majority of the cycle. As a result, within the first positive voltage RF cycle, the target is negatively charged, and during the rest of the cycle a steady flow of positive ions to the target occurs. During the negative voltage cycle, there is insufficient time for the positive ion flow to completely neutralize the negative charge at the target surface. In effect, the target “self-biases” to a negative voltage and facilitates sputtering by positive ion bombardment. An important feature of RF sputtering is that electrons in the plasma acquire sufficient energy to cause ionizing collisions, and hence reduce the requirement of secondary electrons to sustain the plasma.

RF power is supplied by a physically separated RF generator that is coupled to the vacuum chamber by a coaxial cable. A matching network is used to transform the
discharge impedance to the cable impedance (maximize power transfer from the RF generator to the plasma), because the electrical impedance of the RF discharge is usually much lower than the cable impedance (~50 Ω). Commercial RF power supplies consist of two separate units, the RF generator and the tuner. The tuner is an electromechanical apparatus based on the matching network circuit, which transform the electrical load impedance of the plasma to a constant resistance R at the output of the RF generator.

One of the effects of using ac electricity is that both cathode and anode can be sputtered. The latter is undesirable. To prevent sputtering the anode, the target must be an insulator that is coupled to the RF generator and the area of the target must be small enough compared with that of the anode. The voltage ratio between the cathode and the anode had been related to the area ratio by [26]

\[
\frac{V_c}{V_a} = \left(\frac{A_a}{A_c}\right)^4
\]

(2.5)

where \(A_a\) and \(A_c\) are the area of the anode and the cathode, respectively.

RF sputtering has been widely used to sputter deposit insulating thin films such as SiO\(_2\), Al\(_2\)O\(_3\), BN, SiC, and Si\(_3\)N\(_4\) [27]. While the high dielectric constant materials are attractive for capacitors, the low dielectric constant materials are useful for thin films circuit and for protective coating applications.
Magnetron sputtering

Magnetron sputtering system was developed by Penning [28] using a cylindrical hollow magnetron configuration. The process was further developed by Kay and others [29],[30] resulting in the development of the planar magnetron configuration and the cylindrical magnetron source by Penfold and Thornton [31].

In the presence of only a uniform magnetic field, the electron drifts along field lines in a helical trajectory with a fixed gyro (or Larmor) radius and gyro (or cycletron) frequency. If a uniform electric field parallel to the magnetic field is applied, the electron trajectory changes such that, while accelerating in the electric field, the helix pitch increases with time. If the electric and magnetic fields are made perpendicular to each other, the electron will trace a cycloidal orbit. This behavior of electrons is used to extend the time spent by electrons within the plasma, thus enhancing the efficiency of the ionization process at much lower pressures than in diode sputtering processes. A schematic diagram of a planar magnetron configuration is shown in Fig. 2.5. A series of bar magnets are arranged in such a fashion as to form closed loop field lines. At some point in the closed loop path, the magnetic induction component perpendicular to the target surface is 0 whereas the parallel component is at a maximum. At this location, the net magnetic induction is perpendicular to the electric field, which is perpendicular to the target surface. The locus of these points over the target surface represents the points of maximum erosion of the target. Electrons are initially ejected perpendicular to the target with energies of around 5 eV and follow a helical trajectory. Once the region of the parallel magnetic field is encountered, the electrons are vent back towards the target. The net motion of the electrons consists of a cycloidal trajectory around the erosion track.
Fig. 2.5 Schematics of planar magnetron sputtering.
The increases ionization efficiency during DC magnetron sputtering facilitates an order of magnitude decrease in sputtering pressures compared with diode sputtering. Deposition rates for planar magnetron sputtering are higher than those obtained with diode sputtering. Vorous reported deposition rates of up to 1 µm min$^{-1}$ for Al [32]. Magnetron sources operate at cathode potentials ranging from 300 to 700 V, with current densities from 4 to 60 mA cm$^{-2}$, and power densities varying from 1 to 50 W cm$^{-2}$ [21].

The arrangement of the magnets is dictated by geometrical considerations, the requirement of closed loop field lines and an adequate maximum value of the parallel magnetic induction component for sputtering at the desired pressure. Commercially available magnetron modules are also working on methods of optimizing target utilization. The approaches being explored include improved design of the magnetic induction profile and target geometry.

Sputtering targets are usually attached to the water-cooled cathode body, using solders or epoxies. In some cases, the target is directly in contact with cooling water. In such situations, the target is mechanically clamped to the cathode body and dark space (or ground) shield shielding acquires considerable importance. The function of the dark space shield is to prevent sputtering of the fixtures used to clamp the target or the target assembly itself. In addition, the shield has also helped to minimize the arcing that occurs at the cathode edges. The shield should be located at a distance less than the cathode dark space thickness in order to eliminate the possibility of creating plasma between the cathode and the shield.

The thickness uniformity of magnetron sputtered films follows a typical cosine law to be explained later in the sputter yield section [33]. Some of the approaches, which
have been tried to minimize thickness variation including controlled substrate motion, modified magnetic modules and the use of special shielding arrangements adjacent to the cathode or the substrate.

**Reactive sputtering**

The combination of DC or RF sputtering with the introduction of reactive gas species such as N\textsubscript{2}, O\textsubscript{2}, or CH\textsubscript{4}, mixed with Ar, is often used to synthesize compound films, TiN, CrN, Al\textsubscript{2}O\textsubscript{3}, or TiC, on the substrate. This group of process is called reactive sputter deposition. The deposited film is either a solid solution of the target material doped with the reactive component, stoichiometric compound, or a mixture of a target material and stoichiometric compound. The main advantages of reactive sputtering are that complex compounds can be produced using metallic target, insulating compound can be deposited with DC power supplies, and graded compositions can be produced. The main problem with reactive sputtering is the potential difficulty in controlling the process due to its complexity. Compared with reactive evaporation, an additional complication of reactive sputtering is the possibility of compound forming reactions occurring at the target surface. The relationship between the properties of the film and the rate of reactive gas injection is usually non-linear and very strongly dependent on the configuration of the sputtering unit and has been reviewed [34]~[37].

2.2.3 Sputter yield

The sputtering process is quantified in terms of the sputter yield, defined as the number of target atoms removed from the target surface per incident particles [38].
Sputtering is the interactions of incident particles with target surface atoms. The sputter yield will be influenced by energy of incident particles, target materials, incident angles of particles, and crystal structure of the target surface. Using the analogy of elastic collisions in the game of pool, sputtering theory had been developed based on the concept of elastic binary collisions [20]. The sputter yield, \( S \), of a given material bombarded with different element is given by

\[
S = k \left( \frac{1}{\lambda(E) \cos \theta} \right) \left( \frac{M_1 M_2}{M_1 + M_2} \right) E \quad (2-6)
\]

where, \( k \) is a constant which include different target material constants, \( \lambda(E) \) is the mean free path for elastic collisions near the target surface, \( \theta \) is the angle between the normal on the target surface and the direction of the incident ions, \( M_1 \) and \( M_2 \) are the masses of the incident ions and target atoms, and \( E \) is the energy of incident ions. Fig. 2.6 shows experimentally determined sputter yields as a function of atomic number when \( \text{Ar}^+ \) ion is used as a sputtering gas [39].

The importance of the sputter yield lies in the fact that it determines the erosion rates of sputtering targets and to a large degree, the deposition rates of sputtered films. Some factors, which are not considered in the simplistic model presented above, are

1. Bombarding ions are not necessarily monoenergetic;
2. Sputter yields for pure elements cannot be used to assess the performance of alloy, compound, or composite targets;
3. For compound/composite targets, dissociation reactions are usually neglected, although they could have a significant effect on sputter yields;
Fig. 2.6 Sputter yield vs. atomic number for the impingement of Ar⁺ [38].
4. Sputter yield data can be altered considerably by variations in target characteristics (e.g. grain size, texture, area fractions of different phases, temperature, etc.);

One of important advantage of sputtering process is the possibility of depositing multicomponent films with the same composition as the target, despite the different sputter yields of the constituent elements. The explanation for this feature of sputtering processes goes as follows. Initially. The element with a higher sputter yield is preferentially removed from the target surface, creating an “altered layer”. Further bombardment of the target surface, depleted of the higher sputter yield element, results in sputtering of the lower sputter yield element. Finally, a steady state situation is reached, when the target stoichiometry is reproduced in the growing film. It should be noted that development of an “altered layer” requires that no solid state diffusion occurs in the target. Consequently, the target must be adequately cooled, in order to minimize heating of the target.

2.3 Mechanical Properties and Microstructure of Thin Films

In any applications, mechanical properties and adhesion strength of thin films are one of the most important properties. During the growth, large residual stresses are developed in thin films [42],[43]. The magnitude of the stress is comparable to the yield strength of most bulk materials. Sometimes, the stress generated during the growth is sufficient to overcome the adhesion between the film and the substrate, and results in peeling of the film from the substrate. Microstructure of thin films and stresses in thin films are described in the following.
2.3.1 Structure zone model of thin films

The atom condensation process during sputter deposition can occur in three steps. The first step is that incident atoms transfer kinetic energy to the lattice and become loose bonded adatoms. The second step is the diffusion of adatoms on the surface. In this stage, adatoms exchange energy with the lattice and other adsorbed species until they are either desorbed or become trapped at low energy lattice sites. The final step is that incorporated atoms readjust their positions within the lattice by bulk diffusion process. These four steps can be quantified in terms of the characteristic roughness of the coating surface, the activation energies for surface and bulk diffusion, and the sublimation energy. For many pure metal these energies are related and proportional to the melting point of the metal. Thus various basic processes can be expected to dominate over different ranges of $T_s/T_m$. $T_s$ and $T_m$ represent the substrate temperature and the coating material melting temperature, respectively. The mechanical strength of the thin film depends on the microstructure of the coating. The mobility of adatoms or clusters increases with increasing substrate temperatures, which favors grain growth, recrystallization, and an increasing order of the microstructure. Movchan and Dechisin also proposed a structure zone model as a function of $T_s/T_m$ [21],[44]. The morphological structure of the coating is related to $T_s/T_m$, which explains the thermally induced adatoms mobility.

Thornton developed the structure zone model of thin films (Fig. 2.7) based on the ratio of the substrate temperature and the coating materials melting temperature, and sputtering gas pressure [45]. Thornton’s structure zone model is independent of the particular method of vapor deposition and can be applied to metal and ceramic crystalline and amorphous films with thickness over 20 nm [46],[47]. The pressure dependence is
Fig. 2.7  Schematic representation of the influence of substrate temperature and argon pressure on the structure of metal coatings.  $T$ is the substrate temperature and $T_m$ is the melting point of the coating material [19].
believed to result because collisions between sputtered atoms and argon atoms at high argon pressure cause the coating atoms to arrive at the substrate in randomized directions that prompt shadowing. This is a simple geometric interaction between the roughness of the growing surface and the angular directions of the arriving coating atoms.

Thornton’s structure zone model is divided in four sections, zone 1, zone T, zone 2, and zone 3. Zone 1 structure results when the adatom diffusion is not sufficient to overcome the effects of the shadowing. This zone forms at low substrate temperature (i.e. low $T_s/T_m$) and is promoted at high sputtering gas pressure. It is usually consists of tapered grains with domed tops which are separated by voided boundaries. The grain size increases with the increasing substrate temperature.

Zone T was introduced by Thornton and is identified to be not a separated zone but rather a lower sub zone within zone 1. The microstructure in zone T region shows a dense fibrous structure with a smooth and highly reflective surface. Zone T also forms at low substrate temperature when the coating flux arrives in a direction that is highly normal to the substrate surface. Thus shadowing effects are minimized. Coatings with the zone T structure are desired for decorative coating applications. Large intrinsic stress is generated in the zone T region.

2.3.2 Internal stresses

The internal stresses in films also have considerable offer on the microstructural, mechanical and adhesion properties of films. The residual stress in a film consists of two major components, an intrinsic stress resulting from the lattice mismatch between the
substrate and coatings, and a thermal stress arising from the difference in the thermal expansion coefficients of the film and the substrate [48].

**Intrinsic stress**

The intrinsic stress might be resulted from the difference in lattice constants between adjacent layers, the interaction of growing domains of grains and the plastic deformation on the substrate surface due to atom bombardments. Although the magnitude of these stresses can be very high, often exceeding the yield strength of the bulk material, these stresses can be released after annealing [49]. For low melting point materials, the deposition conditions will generally involved sufficient high value of $T_s/T_m$ so that the intrinsic stresses are significantly reduced by recovery during the coating growth. Higher melting point materials are generally deposited at relatively low $T_s/T_m$ (< 0.25) so that the intrinsic stress dominate over the thermal stresses. For thin films (< 5000 Å) the intrinsic stresses are generally constants through out the coating thickness. They are typically compressive for sputtered metal coatings.

**Thermal stress**

When films are prepared by means of deposition on a hot substrate or by thermal decomposition, differences in the contraction of the film and the substrate, which mainly appear during cooling of the system, develop a thermal residual stress in the coating. The thermal stress of a thin film on a relatively thick substrate may be expressed as [50]

$$\sigma_c = \frac{\Delta \alpha \Delta T E_c}{1 - \mu}$$  \hspace{1cm} (2.7)
where $\sigma_c$ is the residual stress in the coating, $\Delta \alpha$ is the difference in coefficients of thermal expansion, $\Delta T$ is the temperature drop, $E_c$ is the Young’s modulus of the coating, and $\mu$ is the Poisson’s ratio for the coating. The thermal stress is evidently significant when intrinsic stress is negligible. Films of low melting metals as well as those with a high state of structural order show little intrinsic stress, and thermal stress is therefore the main contribution to the residual stress in these cases.

The interfacial bond must withstand the shear forces associated with the accumulated intrinsic stresses throughout the coating, as well as the thermal stresses. Since the intrinsic stress contribution increases with increasing coating thickness, it can be the cause of premature interface cracking, and poor results in adhesion tests, for coatings with thickness exceeding critical values, which may be as low as 1000 Å.

2.3.3 Adhesion

The adhesion strength of a coating depends on both the bonding strength between the coating and substrate materials and the microstructure in the interface. The bonding may be chemical, van der waals, electrostatic, or combination of these three types. Chemical bonds are the strongest but require that atoms are appropriate positions to share electrons. Van der waals bonds arise from polarization interactions. They do not require intimate atomic contact, but weaker than chemical bonds. Electrostatic bonds result from charge double layers between the coating and substrate, and for some metal insulator interfaces, may have strengths comparable to van der waals bonds.
One of the techniques to measure the adhesion strength is the scratch test. In a scratch test, a smoothly rounded stylus travels across the film surface. The vertical load on the stylus is increased until the film is stripped from the substrate. The tangential force on the stylus tip is also measured during testing.

As the stylus moves, the coating deformed to contour to the shape of the indenter, causing stretch of the film and the development of a shear force between the film and the substrate surface. This shear force would have a maximum value at the tip of stylus. At the critical load, the shear force that combines the residual stresses in the film and applied shear force from the stylus, at the tip would be sufficient to break the adhesive bonds between film and substrate.

The critical load is determined by both adhesion and the mechanical strength of the film. However, the critical load also depends on several other parameters, such as substrate hardness, coating thickness, surface roughness, coating hardness, loading rate, indenter tip radius, and friction between the costing and the indenter [51]-[54]. Some of them are directly related to the test itself, others are related to the coating/substrate combination.

In spite of these complications, however, the scratch test is often used for several reasons: (a) it provides relative bonding strength values, particularly for films on the same substrate, or the same film/substrate system, (b) reproducible, quantitative critical loads can usually be defined for brittle film, and (c) the scratch test can be used for a variety of adherent film/substrate systems.

2.3.4 Hardness
Hardness test of coatings is a relatively simple method of film characterization. The Vickers and Knoops hardness tests are commonly used. The Vickers hardness test employs an indenter consisting of a square-based diamond pyramid ground to have a face angle of 136°. The Koops hardness test employs a rhombic-based diamond pyramid indenter where the diagonal length ratio of the major to minor diagonal is 7.11. The penetration depth is four times of minor diagonal length for Koops and 7 times of diagonal length for Vickers.

Testing loads are selected to produce an indent whose lateral dimensions are large enough to be measured with an optical microscope. The penetration depth should be small enough compared with the film thickness. However, the plastically deformed zone under the indenter might extend to the substrate and the measured hardness value may include the effect of the substrate material. Hardness comparison should, therefore, only be made when testing methods and film thickness are maintained approximately constant.

2.4 Heat Treatment of Thin Films

Heat treatment at temperatures higher than deposition temperature increases the crystalline size. Generally the crystallite size of films increases with an increasing deposition temperature. Most metal films deposited at ambient temperature are amorphous. The growth effect of heat annealing at higher temperature than the deposition temperature is different from that obtained by using the same temperature during the deposition. The difference between two cases arises from the high-activation-energy process of thermal diffusion of surface atoms of a condensate in high temperature
annealing as compared with the orderly process of condensation of mobile adatoms in the latter case.

Structural changes in films on annealing have been investigated by using electron microscopy and x-ray diffraction techniques. Generally, the crystallite size increases as a result of a sintering process of the crystallite in contact. The driving force is provided by the tendency to minimize the total surface energy. Niu et al. [55] and Pop et al. [56] have investigated effect of heat treatment of films. The microstructure of the films annealed at a temperature higher than deposition temperature consists of larger crystallite size. Staia et al. [57] studied effects of heat treatment on microstructure and mechanical properties of electroless deposited Ni-P films. It has been found that an increase in annealing time and/or temperature produced an increase in the size of precipitates. Hardness decreases with increasing temperature together with an excessive heating time.
3. EXPERIMENTAL PROCEDURE

This chapter consists of four sections. In the first section, Si wafer and steel substrates preparation used in this thesis are explained. The second section describes pulsed DC reactive sputter deposition of Cr/CrN including schematic of DC sputter deposition unit. The third section explains rapid thermal processing (RTP) in an infrared (IR) furnace. In the fourth section, the characterization techniques used in this thesis are described.

3.1 Substrate Preparation

Cr and Cr nitrides were deposited on commercially available 1010 Steel (Zinc coated steel, Kocour Company, Chicago, IL) and Si (100) wafers. The dimensions of steel coupon specimens were approximately 17.8×17.8×0.3 mm. The Zn layer on the steel substrate was removed by using a 15 % HCl solution for 5 min. The steel substrates were cleaned with distilled water. Both Si (100) wafer and steel substrate were further cleaned with acetone, and methanol in an ultrasonic cleaner for 20 min. and then dried by blowing with pressurized oxygen.

3.2 Sputter Deposition

A pulsed DC magnetron sputter deposition system was used to deposit Cr/CrN thin films in this study. The deposition system and procedures are described below.

3.2.1 Deposition unit
The coatings were deposited using a sputter deposition unit in conjunction with a pulsed DC magnetron power supply (Cooke Vacuum Product, Norwalk, CT). The unit has four US guns for mounting targets and is shown in Fig. 3.1. The pulsed DC plasma generator RPG-50 (ENI, Rochester, NY) with a frequency of 185 kHz and duty cycle of 96% was used to deposit Cr/CrN coatings in this study. The RPG-50 has the maximum output power of 10 kW (maximum output voltage of 500 V). The applied power was determined by multiplying the average applied voltage and the average current during the deposition cycle. These power and voltage are displayed on the front display panel of the pulsed DC plasma generator RPG-50 unit. The applied voltage during a typical deposition condition was found to be 340 V for the deposition power of 200 W. Hence, the ion current at the target is 13 mA cm\(^{-2}\) at 200 W approximately. It is to be noted that the voltage and ion current depend on the parameters such as the plasma composition and total pressure. The magnetron is realized by a ring shape permanent magnet placed in the gun behind the target attachment surface. The gun is cooled by deionized water with the minimum specific resistivity of 15 M\(\Omega\) cm\(^{-2}\). The resistance between the gun and the substrate and the gun and the chamber is about 1 M\(\Omega\) when the specific resistivity of the cooling water is proper. The chamber and the substrate are held at the ground potential during deposition.

After placing substrates in the chamber, vacuum is drawn in the chamber using a mechanical rotary pump and a CT-8 cryogenic pump (CTI Cryogenics, Mansfield, MA). The rough and final pressures in the chamber were monitored by using a thermocouple (TC) gauge and an ion gauge, respectively. The pumping speed of the CT-8 cryopump is
Fig. 3.1  Schematic of vacuum chamber for four-gun Pulsed DC magnetron sputter deposition.
1.5 m³ sec⁻¹ (1500 l sec⁻¹) of air. The crossover value (CV), which is the gas burst rating of cryopump, is 19.95 Pa-m³ (150 Torr-liters). The condensable gas capacity is 1 m³ (1000 liter) for argon, nitrogen, oxygen, etc. and 0.012 m³ (12 liter) for hydrogen at 6.7×10⁻³ Pa (5×10⁻⁶ Torr) hydrogen partial pressure. The maximum argon throughput is 700 SCC min⁻¹. The crossover pressure (CP), that is the pressure in a vacuum chamber when the cryopump high vacuum pumping starts, is set to 20 Pa (150 mTorr) for the deposition unit. The nominal value of CP is usually determined by dividing the specified CV by the chamber volume. A slightly higher crossover pressure than the nominal CP is desired to prevent back streaming. The optimum value for a particular system is the one that causes a slight increase in temperature with rapid recovery.

3.2.2 Vacuum and back filling

Typically, the base vacuum was around 2×10⁻⁴ Pa (1.5×10⁻⁶ Torr), which can be achieved in two stages. The mechanical pump achieved a pressure of 20 Pa (150 mTorr) in 5 min. At this time, the high vacuum valve opens and the pressure in the chamber is dropped instantaneously to less than 0.003 Pa (2.25×10⁻⁵ Torr). Typically, about 20 min is required to reach the base vacuum of 2×10⁻⁴ Pa (1.5×10⁻⁶ Torr). During this time, the substrate and the chamber walls were outgasing.

After reaching the desired base vacuum the throttle valve is activated and the chamber is back filled with argon. The total pressure of argon (or argon plus nitrogen in the case of reactive sputter deposition) is maintained at the pressure of 1.333 Pa (10 mTorr) for all the depositions. Ultra high purity (UHP) argon was used for sputtering. The sputtering gas compositions were controlled by two flowmeters, one each for argon
and nitrogen. The nitrogen gas percentage is reported in terms of percentage by volume.
The flowmeters were calibrated using soap water and graduated pipette (bubble method)
prior to usage. The flow rate of argon (or argon plus nitrogen) to maintain 1.34 Pa (10 mTorr) pressure was found experimentally. After the pressure in the chamber came close to 1.34 Pa (10 mTorr), the plasma was initiated.

3.2.3 Pre-sputtering and deposition

Before each deposition, pre-sputtering was done for 1 hr with ultra high purity argon as the sputtering gas to remove any nitrides/oxides from the target surface. During the pre sputtering, the target surface formed a stable altered layer and the applied power was stabilized. In this stage, the shutter is kept closed while sputtering was being carried out. Atoms or clusters sputtered from the target, therefore, deposit on the shutter and not on the substrate.

After pre sputtering, the shutter is opened and the deposition is initiated. Usually, the time of deposition is controlled to obtain the required thickness based on the experimentally determined deposition rates. However, the sputter deposition unit is equipped with a STM-10C quartz crystal vibrating thickness monitor (Sycon Instruments, Syracuse, NY) that can be used to measure approximate thickness of the deposited coating layer. It is noted that the deposition rate also depends on the power, sputtering gas pressure, and target-to-substrate distance. For all deposition, the sputtering power was maintained at 200 W. A target-to-substrate distance of 8.4 cm was maintained during all the depositions.
All the depositions were carried out at a total pressure (argon plus the reactive gas) of 1.333 Pa (10 mTorr) and at 200°C, which was maintained by a substrate heater with nichrome wire resistance heating. The temperature was monitored with a K-type (chromel-alumel) thermocouple placed below the substrate. The substrate is in contact with the substrate heater via silver paste applied on the bottom of the substrate.

3.3 Rapid Thermal Processing (RTP)

Deposited samples were heat treated in an infrared (IR) furnace. A set of coated samples were placed in a graphite crucible and then introduced in the IR furnace. The chamber was evacuated and purged with argon gas. Argon flow rate was kept at 6 liter min\(^{-1}\) during the heat treatment. Samples were annealed at 400°C for 2 min. Temperature was monitored by using a K-type thermocouple attached on the graphite crucible. The heating rate was found to be 9.3°C sec\(^{-1}\).

3.4 Characterization

3.4.1 Film thickness

The thickness of the films was measured using a Dektak II profilometer (Veeco, U.K). During deposition, a dummy sample with a small area masked was placed along with the sample on the substrate holder. The dummy sample was a large piece of silicon wafer with a small piece of silicon wafer glued on the top to mask deposition in a small area. After deposition the top piece is removed to form a step on the lower Si wafer, which consists of uncoated silicon wafer and the coating. A sensitive diamond stylus is made to move across the silicon wafer surface that has the step. The vertical movement, as it
crosses the step, is measured by a piezoelectric sensor and amplified to give the step height, which is equivalent to the thickness of the deposited film. By this technique, thickness down to 0.5 nm can be sensed with a maximum vertical range of 65.5 µm and up to 2000 data points per scan. An average of four readings was taken for each sample. Scanning electron microscope (SEM) was also used to measure the thickness of the coating. From the cross section image of the coated Si wafer and steel sample, thickness of the coating was measured. An average coating thickness was determined and reported in this study.

3.4.2 Microhardness

Microhardness of the films was determined by using a M-400-H1 microhardness tester from LECO. A Vickers indenter was used for all microhardness test in this study. An average of ten readings was taken for each sample. A dwelling time of 20 sec and loads between 25 g-force and 200 g-force were used for the measurement. The indent diagonals were measured with an optical microscope at a magnification of 400 times. It is noted that the use of very low load generates large error in microhardness value since the diagonal length of indent is too small to measure accurately.

3.4.3 Scratch test

The adhesion between the coating layer and the substrate and the critical force, at which the coating fails, were examined by using a Sebastian V scratch tester (Quad Group, Spokane, WA). The apparatus consists of a vertically aligned spherical diamond stylus that is in contact with a deposited sample as shown in Fig. 3.2. The sample stage
Fig. 3.2 Schematic of the scratch test setup.
moves horizontally along with the sample at a predetermined scanning rate. An increasing normal load, starting from zero, is applied on the stylus (diamond tip with a 533 µm in radius) at a predetermined loading rate. Each sample was scratched three times. Computer logged data obtained from the scratch test include applied load, transverse force, friction coefficient, and acoustic emission signal, which is detected by a piezoelectric acoustic transducer mounted on the stylus arm. The acoustic signal generated during the scratch test was recorded in order to identify the critical force. A burst in the acoustic signal indicates either debonding or cracking of the coating. The normal load corresponding to these phenomena is known as the “critical load”. The scratch tracks on the films were examined by using an optical microscope. During the scratch test, the loading and scan rates were maintained at 0.03 cm sec\(^{-1}\) and at 0.04 kgf sec\(^{-1}\), respectively. The maximum load and travel distance were fixed at 3 kgf and at 3 cm, respectively. The scratch test stops at the time either the load or travel distance reaches its maximum. The scratch track was also examined under an optical microscope. From both computer logged data and scratch tracks, the critical load was determined for each sample.

3.4.4 X-ray diffraction analysis

X-ray diffraction (XRD) analysis was performed to determine the phases present in the coatings by using a Phillips diffractometer with Cu K\(_{\alpha}\) radiation, Ni filter, and a scanning speed of 0.04° per sec. The main characteristics of an X-ray diffraction pattern are the intensity, position, and full width at half maximum. The intensity of a diffraction pattern indicates the quantity and preferred orientation of the phase present in the sample.
From the peak position and shape of the diffraction pattern, lattice strain and crystalline size can be determined.

3.4.5 Scanning electron microscope

A Hitachi field emission scanning electron microscope (SEM) was used for verifying the thickness of coatings by secondary electron image. The fractured cross section of coated samples was examined by using SEM for the microstructure of the coating layers. Energy dispersive spectroscopy (EDAX), which is attached to the Hitachi SEM unit, is used to determine the composition of the coatings.
4. RESULTS AND DISCUSSION

This section consists of two parts. In the first part, the structure and mechanical properties of the reactively sputter deposited Cr/CrN coatings on 1010 steel are described. The deposition rate, grain size, microhardness and adhesion strength of Cr/CrN thin films deposited at 200°C with 0, 3, 5, and 7% nitrogen contents in the sputtering gas are covered. In the second part, the effects of surface preparation and rapid thermal process (RTP) on the sputter deposited Cr/CrN coatings on steels are described. Coating properties such as microhardness, and adhesion strength are reported.

It should be noted that the first part is focused on the investigation of the structure and mechanical properties of Cr/CrN films deposited using DC magnetron sputter deposition at 200°C and different nitrogen contents in the sputtering gas. The second part is focused on the adhesion strength of rapid thermal processed Cr/CrN films on 1010 steel substrates.

4.1 Cr/CrN Coatings Deposited Using DC Planar Magnetron Sputter Deposition

In this section, the sputter deposition rate, microstructure and mechanical properties, including adhesion strength, of reactively sputter deposited Cr/CrN thin films on steel substrates as a function of the nitrogen content in the sputtering gas were described in detail.

4.1.1 Sputter deposition rate

To determine the deposition rate and examine potential initial incubation period of deposition during each deposition, a series of experiments was done on steel
substrates. With identical deposition conditions except the processing time, Cr films were sputter deposited on 1010 steel substrates. The chamber was evacuated to around \(2.66 \times 10^{-4}\) Pa (\(2 \times 10^{-6}\) Torr), and the Ar pressure of 1.333 Pa (10 mTorr) was maintained during the deposition. The substrate temperature was at 200°C and the deposition power and voltage were 200 W and 340 V, respectively. With 0% nitrogen in the gas, a series of Cr deposition were done for 60, 90, 180, and 300 min and with 3, 5, and 7% nitrogen in the gas only for 60 and 90 min. The distance between the substrate and the target was 8.4 cm for all the depositions. Pre-sputtering was performed for 30 ~ 60 min before sputter deposition, depending on the target surface condition. It has been observed that the plasma color reflects the condition of the target surface. At the beginning of pre-sputtering, plasma color was red and deposition rate was very low. With increasing pre-sputtering time, the plasma color changed to blue and the deposition rate was increased. The thickness of Cr films as a function of deposition time was shown in Fig. 4.1. The deposition rate of Cr was found to be 1.23 \(\mu\)m hr\(^{-1}\) with pure Ar. The linear relationship between the coating thickness and the deposition time suggests that under the present deposition condition, there is no incubation time for deposition.

As shown in Table III, the deposition rate appeared to be independent of the nitrogen contents up to 7% nitrogen in the sputtering gas. The deposition rates of Cr with 3, 5, and 7% nitrogen were 1.19, 1.22, and 1.22 \(\mu\)m hr\(^{-1}\), respectively.

4.1.2 Structure of films

The XRD patterns of the Cr/CrN coatings on Si (100) substrates are shown in Fig. 4.2. The body-centered cubic (BCC)-Cr phase was detected in all coatings and the
Fig. 4.1 Deposition rate of Cr with pure Ar as a sputtering gas at a power of DC 200W on steel substrates.

\[ y = 1.23x \]
Table III  Sputter deposition rate at different nitrogen contents in the sputtering gas.

All samples were deposited at DC 200W, 185 kHz, and 96% duty cycle.

<table>
<thead>
<tr>
<th>N₂ Content (vol.%)</th>
<th>Thickness (μm)</th>
<th>Deposition Time (min)</th>
<th>Deposition Rate (μm hr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.01</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.92</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.67</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.16</td>
<td>300</td>
<td>1.23</td>
</tr>
<tr>
<td>3</td>
<td>1.18</td>
<td>60</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td>1.85</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.20</td>
<td>60</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>1.93</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1.09</td>
<td>60</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>1.89</td>
<td>93</td>
<td></td>
</tr>
</tbody>
</table>
face-centered cubic (FCC)-CrN phase was detected only when nitrogen gas existed in the sputtering gas. The hexagonal closed packed (HCP)-Cr$_2$N phase is not detected in any coatings. With increasing nitrogen contents in the sputtering gas, the intensity of FCC-CrN (200) peak was increased.

As shown in Fig. 4.2, the peak broadening effect of Cr and CrN coatings was observed. Such broadening effects may be caused by the small grain size and the lattice strain [58]. The peak full width at half maximum (FWHM) was measured for Cr (110) and CrN (200) peaks. The average grain size of Cr and its nitride coatings can be calculated using Scherrer’s equation [59]

$$d = \frac{0.94 \lambda}{B(2\theta) \cos \theta}$$

(4.1)

where, d is the crystal dimension perpendicular to the reflecting plane, $\lambda$ is the wavelength, and B(2$\theta$) is FWHM. The measured FWHM was found to be 0.02° of 2$\theta$ for the Cr (110) peak. Using this equation, the calculated grain size of the Cr phase for the sputter deposited Cr coating was in the range of 7 to 8 nm. The grain size for the CrN phase in the coating cannot be calculated using the Scherrer’s equation because the peak is too diffused to correctly calculate the FWHM of the diffraction pattern. Scanning electron microscope (SEM) was used to examine the cross sectional of the coatings (Fig. 4.3) deposited with various nitrogen contents. All coatings show the columnar microstructure clearly. The coating thickness determined by the profilometer agrees with those measured from the SEM images.
Fig. 4.2  X-ray diffraction patterns of Cr and Cr/CrN coatings deposited on Si (100) wafer at 200°C with 0, 3, 5 and 7% N₂ in the gas.
Fig. 4.3 Cross section images of Cr and Cr/CrN coatings deposited at 200°C on Si (100) wafer with (a) 0, (b) 3, (c) 5, and (d) 7% N₂.
The relative intensities of Cr (110) and CrN (200) peaks for each coating indicate the relative amount of Cr and CrN in the coating. It is found that the volume fraction of CrN phase increases with increasing N2 contents in the sputtering gas while that of Cr phase decreases. From the relative intensities of Cr (110) and CrN (200) peaks, the volume fraction of CrN phase in the coating has been calculated and is shown in Fig. 4.4. It is shown that the volume fraction of CrN phase in the coating increases from 0.31 at 3% N2 to 0.49 vol.% at 7% N2 in the sputtering gas.

4.1.3 Stability of Cr, Cr2N, and CrN

As reported previously, no Cr2N phase appeared in X-ray diffraction patterns although the phase diagram of the Cr-N binary system shows existing of Cr2N (Fig. 4.5) [60]. To determine the stability of Cr, Cr2N, and CrN phases, thermodynamic analysis was performed. The standard Gibb’s free energy of formation of CrN and Cr2N are obtained from Kubaschewski and Alcock [61]

\[
2Cr_{(s)} + N_{2(g)} = 2CrN_{(s)} \quad (4.2)
\]

\[
\Delta G^0 = -242462 - 48.17 \log T + 359.1T \ J/mol \quad (4.3)
\]

\[
4Cr_{(s)} + N_{2(g)} = 2Cr_2N_{(s)} \quad (4.4)
\]

\[
\Delta G^0 = -217149 - 48.17 \log T + 317.7T \ J/mol \quad (4.5)
\]

For stability comparison, the Gibb’s free energy of mixing from elements Cr_{(s)} and N_{2(g)} based on per mole of the binary system must be calculated for each phase. Fig. 4.6 shows the calculated free energy of mixing, G^M, for composition N = 0.33 and 0.5 at
Fig. 4.4  Relative intensities of Cr (110) and CrN (200) peaks deposited with 0, 3, 5, and 7% N₂ in the gas at 200°C. Volume fraction of Cr and CrN phases are shown at top of the bar.
Fig. 4.5. The Cr-N binary system phase diagram [60].
200, 400, 600, 800, and 1000°C where N is the atomic (mole) fraction of nitrogen in the
Cr-N binary system. At 200°C, $G^M$ for $\text{Cr}_2\text{N}$ is higher than the combination of ($\text{Cr} + \text{CrN}$), indicating that $\text{Cr}_2\text{N}$ is not stable reference to the ($\text{Cr} + \text{CrN}$) combination. Hence, the phases occurring at 200°C are $\text{Cr}$ and $\text{CrN}$. Similar situation holds for the stability of phases at 400°C although the free energy data suggests that $\text{Cr}_2\text{N}$ is approaching equilibrium with ($\text{Cr} + \text{CrN}$). At 600, 800, and 1000°C, all $\text{Cr}$, $\text{CrN}$, and $\text{Cr}_2\text{N}$ phases are stable. As shown by the relative $G^M$ values of each compound, such thermodynamic analysis matches well with the results obtained in this study and those reported previously [13]~[15].

The phase diagram of the Cr-N binary system reported in the literature [60],[62]~[64] do not include region below 500°C. Based on thermodynamic stability analysis shown above and experimental results in this study, it is believed that the $\text{Cr}_2\text{N}$ phase is not stable below 400°C. Somewhere around 400°C, the eutectoid reaction

$$\text{Cr}_2\text{(s)} + \text{CrN}_2\text{(s)} = \text{Cr}_2\text{N}_2\text{(s)}$$  \hspace{1cm} (4.7)

exists. By allowing $G^M$ for $\text{Cr}_2\text{(s)}$, $G^M$ for $\text{Cr}_2\text{N}_2\text{(s)}$, and $G^M$ for $\text{CrN}_2\text{(s)}$ into a straight line in the $G^M$ vs. composition diagram, the corresponding temperature was found out to be at 430°C. This is proposed to be the eutectoid temperature. From this the portion of the Cr-N phase diagram below 500°C is proposed as shown in Fig. 4.7. Results by Almer et at. [65], Creus et al. [66], and Su et al. [67] agree with this proposed phase diagram. Analysis made here was based on the thermodynamic equilibrium consideration.
Fig. 4.6 The variation of $G^M$ with composition in Cr-N binary system.
Fig. 4.7 Phase diagram of the Cr-N binary system. The phase diagram below 500°C is proposed in this study.
Deposition with extraordinarily high perturbations, such as high bias voltage on the substrate [68] or high deposition power [69], might result in the formation of otherwise unstable phases such as Cr$_2$N. Results reported in the literature also showed that RF magnetron spotter deposition might have facilitated the formation of Cr$_2$N at temperatures lower than that predicted by the equilibrium consideration discussed here.

4.1.4 Microhardness of films

The composite microhardness of Cr and CrN on 1010 steel substrates were measured using a Vickers diamond indenter. Vickers hardness number ($H_V$), defined as the load divided by the surface area of the indentation, was calculated from the following equation [70]

$$H_V = \frac{2L \sin \left( \frac{\theta}{2} \right)}{d^2} = \frac{1.854L}{d^2}$$  \hspace{1cm} (4.8)

where, $L$ is applied load (kg), $d$ is average length of diagonals (mm), $\theta$ is angle between opposite faces of diamond indenter, which is 136°. The applied loads were 25, 50, 100, and 200 g. The hardness of the composite was twice as high as the steel substrate when the nitrogen content in the sputtering is 7% and the load of 25 g is applied. The composite microhardness is summarized in Table IV and shown in Fig. 4.8. It is found that the composite microhardness increases with increasing N$_2$ contents in the gas. Fig. 4.9 shows the dependence of coating hardness as a function of the volume fraction of CrN phase in the film. This quantitative analysis of CrN phase in the coating supports that the amount of CrN phase in the coating is a factor to increase the composite hardness as well as the grain size effect.
Table IV  Hardness (kgf mm\(^{-2}\)) of the substrate and coated steels deposited at 200°C.

<table>
<thead>
<tr>
<th>Load (g)</th>
<th>Substrate</th>
<th>0% N(_2)</th>
<th>3% N(_2)</th>
<th>5% N(_2)</th>
<th>7% N(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>129 ± 3.0</td>
<td>211 ± 3.5</td>
<td>196 ± 5.2</td>
<td>204 ± 4.9</td>
<td>255 ± 10.6</td>
</tr>
<tr>
<td>50</td>
<td>132 ± 0.8</td>
<td>167 ± 2.3</td>
<td>168 ± 2.8</td>
<td>180 ± 2.6</td>
<td>185 ± 4.3</td>
</tr>
<tr>
<td>100</td>
<td>132 ± 0.7</td>
<td>167 ± 3.3</td>
<td>161 ± 2.6</td>
<td>161 ± 2.1</td>
<td>165 ± 1.5</td>
</tr>
<tr>
<td>200</td>
<td>125 ± 1.4</td>
<td>143 ± 2.4</td>
<td>148 ± 3.6</td>
<td>150 ± 2.1</td>
<td>154 ± 1.1</td>
</tr>
</tbody>
</table>
Fig. 4.8  Hardness of the Cr/CrN coatings sputter deposited on 1010 steel substrates with 0, 3, 5, and 7% N₂ in the gas.
Fig. 4.9 The dependence of hardness of coated steels at 50 g-force as a function of the volume fraction of CrN phase in the film.

Substrate (132 ± 0.8 kgf mm$^{-2}$)

Hardness (kgf mm$^{-2}$)

CrN (vol. %)
Many researchers have attempted to calculate the film hardness independent of the thickness of the film and the substrate [71]~[81]. The models used to calculate the film hardness are based on either the deformed area or the plastic zone model. In this study, the film hardness of Cr thin films deposited on various substrates was calculated using Jonsson and Hogmark models (Appendix). The substrates used in this study were Cu, Al, 1010 Steel, Ti-6-4, and Cr. All Cr thin films on various substrates were deposited at the identical condition. Although Cr thin films were deposited on different substrates, film hardness should have identical values because film hardness is independent of the substrate (Table V). However, calculated film hardness on different substrates show different film hardness values on different substrates. It is anticipated that the film hardness is independent of films thickness and substrate. Thus any reported models to calculate film hardness give correct films hardness values. Therefore only composites hardness values are reported in this thesis.

It is shown that samples with Cr/CrN coatings were much harder than the substrate and the composite hardness increases with increasing nitrogen contents in the sputtering gas. An optical micrograph of a typical indent was shown in Fig. 4.10. Cracks were observed around the rim of the indentation. The reported bulk hardness values of CrN and Cr2N are 1100 kgf mm\(^{-2}\) and 1600 kgf mm\(^{-2}\), respectively [15]. The composite hardness showed that the microhardness at a 25 g-force load increases from 211 \(\pm\) 3.5 kgf mm\(^{-2}\) at 0% N\(_2\) to 255 \(\pm\) 10.6 kgf mm\(^{-2}\) at 7% N\(_2\) in the sputtering gas. This corresponds to the formation of the hard CrN phase in Cr phase as well as the solid solution strengthening of the Cr lattice by nitrogen. It also shows that the hardness of the
Table V  Calculated hardness of Cr films on various substrates. All Cr coatings on various substrates were deposited at the identical condition.

<table>
<thead>
<tr>
<th>Load (g)</th>
<th>Cr films on Cu substrate</th>
<th>Cr films on Al substrate</th>
<th>Cr films on Ti-6Al-4V substrate</th>
<th>Cr films on 1010 steel substrate</th>
<th>Cr films on Cr substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Substrate</td>
<td>Composite</td>
<td>Film</td>
<td>Substrate</td>
<td>Composite</td>
</tr>
<tr>
<td>25</td>
<td>109 ± 1.75</td>
<td>127 ± 1.76</td>
<td>790.61</td>
<td>96 ± 1.18</td>
<td>123 ± 2.05</td>
</tr>
<tr>
<td>50</td>
<td>105 ± 1.91</td>
<td>117 ± 1.34</td>
<td>767.93</td>
<td>96 ± 1.16</td>
<td>113 ± 1.35</td>
</tr>
<tr>
<td>100</td>
<td>102 ± 1.18</td>
<td>110 ± 0.81</td>
<td>727.94</td>
<td>94 ± 1.15</td>
<td>105 ± 1.03</td>
</tr>
<tr>
<td>200</td>
<td>101 ± 0.86</td>
<td>106 ± 1.59</td>
<td>706.53</td>
<td>94 ± 1.34</td>
<td>102 ± 1.17</td>
</tr>
<tr>
<td></td>
<td>151 ± 1.47</td>
<td>208 ± 3.87</td>
<td>1835.41</td>
<td>142 ± 1.41</td>
<td>173 ± 4.61</td>
</tr>
</tbody>
</table>
Fig. 4.10  Optical micrograph of a typical indent on Cr/CrN coating on 1010 steel substrate at 200 g-force load.
composite deposited with 0% N\textsubscript{2} was higher than that of the bulk Cr due to the grain boundary effect mentioned in previous section although the hardness of the bulk Cr shows higher hardness value than that of the substrate. Since the sputter deposited Cr and CrN films have the grain size of 7~8 nm, the hardness of Cr films will be higher than that of the bulk Cr. The microstructure of the bulk Cr shows that the grain size of the bulk Cr is around 300 \(\mu\text{m}\) (Fig. 4.11). From the microhardness of the composite, it is shown that the composite hardness increases due to the grain size effect and the formation of the hard CrN phase in the Cr phase as increasing nitrogen content.

4.1.5 Adhesion strength of films

Scratch tests were performed for all coatings to determine the film integrity and the film adhesion. All scratch tracks were examined under an optical microscope. Fig. 4.12 (a), (b) and (c) show scratch tracks and computer logged data of the substrate and Cr/CrN coatings with 0% and 7% N\textsubscript{2} content in the gas. The scratch tracks of Cr coatings deposited with 0% N\textsubscript{2} content in the sputtering gas exhibit transverse cracks inside the scratch track and chips along the scratch track at very early stage of the test. The coatings deposited with 3, 5, and 7% N\textsubscript{2} contents in the sputtering gas show a smooth scratch track instead of a transverse crack at a relatively low load and little broken chips at a relatively high load.

To determine critical loads, the computer logged acoustic signal was examined along with the scratch track image. It is observed that the critical load increases with increasing nitrogen contents in the sputtering gas.
Fig. 4.11 Microstructures of the bulk Cr. It shows the average grain size of 250 µm.
Fig. 4.12  Scratch tracks and typical computer logged data. (a) Steel substrate.
Fig. 4.12   Scratch tracks and computer logged data. (b) Cr films with 0% nitrogen content in the sputtering gas.
Fig. 4.12  Scratch tracks and computer logged data. (c) CrN films with 7% nitrogen content in the sputtering gas.
Critical loads of deposited films with 0 and 7% N₂ in the gas were found to be 0.16 kg and 2.07 kg, respectively. The Critical load increases with increasing nitrogen contents in the sputtering gas because of the formation of CrN phase in Cr phase (Fig. 4.13).

4.2 Comparison of Sputter Deposited Cr Coatings with Electroplated Cr Coatings

Electroplated hard Cr coatings are industrially popular in numerous applications due to their excellent wear and corrosion resistance. As mentioned above, a serious drawback of electroplated hard Cr coatings is the hexavalent Cr emission during production. Sputter deposition, on the other hand, is environmentally safe. There is no hexavalent chromium emission at all. For industrial applications, sputter Cr coatings must perform as good as electroplated Cr coatings in wear resistance. Microhardness is an indication of the mechanical strength and wear resistance of coatings.

To determine the quality of sputter deposited Cr/CrN coatings from this study, microhardness of Cr films coated with electrodeposition was determined and compared with those for sputter deposited Cr/CrN films. Commercially available electroplated Cr coatings on 1010 steel were obtained from the Porter-Guertin Company, Cincinnati, OH. The microhardness of the electroplated Cr coatings (6.92 µm) were measured and compared with sputter deposited Cr coatings (6.16 µm) (Fig. 4.14). At all loads, the hardness of sputter deposited Cr films with 0% N₂ is comparable with that of electroplated Cr films. It is noted that since hydrogen vapor was generated during the electroplating of Cr, the complex hydrides and the cavities were formed in the Cr coatings. Fig. 4.15 shows the optical micrographs of the surface of a sputter deposited
Fig. 4.13  Critical load of Cr/CrN coatings deposited on 1010 steel with 0, 3, 5, and 7% $N_2$ in the gas.
Fig. 4.14  Comparision of microhardness of sputter deposited Cr (6.16 \( \mu \)m) and electroplated Cr (6.92 \( \mu \)m) coatings on 1010 steel substrates.
Fig. 4.15 Optical micrographs of the surface of Cr coatings on 1010 steel. (a) Sputter deposited Cr/CrN film with 7% N₂ in the gas (b) Electrodeposited Cr film.
Cr/CrN and electroplated Cr coatings. These results suggest that sputter deposition can produce Cr/CrN coatings mechanically superior to electroplated hard Cr coatings.

4.3 Effects of rapid thermal process (RTP) in Cr/CrN films on 1010 steel substrates

Reactive sputter deposited Cr/CrN thin films on 1010 steel were heat treated by rapid thermal processing (RTP) in an infrared furnace. Cr/CrN thin films with around 0.5 μm thickness were deposited at 200°C on both as cleaned and 1.0 μm Al₂O₃ polished substrates. From mechanical and structural analysis of Cr/CrN thin films on as cleaned and polished steel substrates, all properties were shown similar results. The only difference between these coatings was that very shiny surface was shown from Cr/CrN coatings on polished substrates. After sputter deposition, samples were heat treated at 400°C in an infrared furnace for 2 min. In this section, mechanical properties and microstructure of as deposited films were compared with heat-treated films. All tested samples were deposited on polished substrates.

4.3.1 Structure of RTP Cr/CrN thin films

The XRD patterns of as deposited and heat-treated Cr/CrN coatings on 1010 steel substrates are shown in the Fig. 4.16 (a) and (b), respectively. It was found that after heat treatment at 400°C for 2 min no extra peaks were detected from both Cr/CrN coatings. HCP-Cr₂N phase was not detected in any coatings after heat treatment. It was also found that either BCC-Cr or FCC-CrN phase has not grown after heat treatment at the present condition. SEM cross section images of Cr/CrN thin films on steel substrates show that
Fig. 4.16  X-ray diffraction patterns of (a) as deposited and (b) heat-treated Cr and Cr/CrN coatings on 1010 steel substrate at 200°C with 0, 3, 5 and 7% N₂ in the gas.
4.3.2 Microhardness of heat-treated Cr/CrN films

Composite hardness of as deposited and heat-treated Cr/CrN thin films on 1010 steel were measured using a Vickers diamond indenter. Measured composite hardness was shown in Fig. 4.18. At a 100 g-force load, as deposited and heat-treated Cr films deposited with 0% nitrogen show 152 ± 3 and 151 ± 0.75 kgf mm⁻², respectively. As deposited and heat-treated CrN films deposited with 7% nitrogen show 155 ± 3.2 and 155 ± 1.8 kgf mm⁻² at a 100 g-force load, respectively. It should be noted that composite hardness might have been influenced by changes the interface between the film and the substrate. However, as mentioned previously, diffusion layer would be very thin and no affecting the composite hardness.

4.3.3 Adhesion strength of as deposited and heat-treated films

Scratch tests were performed for as deposited and heat-treated coatings to determine the film integrity and the film adhesion. All scratch tracks were examined under an optical microscope. Fig. 4.19 (a) ~ (h) show optical micrographs of scratch...
Fig. 4.17  SEM cross sectional images of as deposited and RTP Cr/CrN thin films on 1010 steel substrates.
(e) As deposited CrN film with 5% N₂  
(f) RTP CrN film with 5% N₂

(g) As deposited CrN film with 7% N₂  
(h) RTP CrN film with 7% N₂

Fig. 4.17  SEM cross sectional images of as deposited and RTP Cr/CrN thin films on 1010 steel substrates.
Fig. 4.18 Composite hardness of as deposited and heat-treated Cr/CrN coatings sputter deposited on 1010 steel substrates (a) deposited with 0% nitrogen (b) with 3% nitrogen.
Fig. 4.18 Composite hardness of as deposited and heat-treated Cr/CrN coatings sputter deposited on 1010 steel substrates (c) 5% nitrogen (d) 7% nitrogen. All coatings have thickness in a range of 0.5 to 0.8 µm.
tracks on as deposited and heat-treated Cr/CrN films. Scratch tracks of as deposited Cr/CrN coatings exhibit transverse cracks inside the scratch track and chips along the scratch track at a relatively low load. Heat-treated coatings showed transverse cracks inside the scratch track and chips along the scratch track at a relatively higher load compared to those of as deposited coatings. Fig. 4.20 (a) and (b) show scratch tracks and computer logged data of as deposited and heat-treated Cr/CrN coatings with 3% N₂ content in the gas, respectively. As shown in Fig. 4.20, the scratch track of heat-treated CrN coating showed that transverse crack was generated at higher load than that of as deposited CrN coating. The scratch track of heat-treated coating shows smooth scratch track. It was also found that the coating was removed in less area inside the scratch track than as deposited coating. Cr/CrN coatings with 0, 5, and 7% N₂ contents in the sputtering gas show similar trend in the scratch behavior. The critical load determined from both acoustic signal and optical microscope images are summarized in Table VI.
Fig. 4.19  Scratch tracks of as deposited and heat-treated Cr/CrN films on polished 1010 steel substrate. (a) As deposited Cr films with 0% N$_2$  (b) Heat-treated Cr films with 0% N$_2$. 
Fig. 4.19 Scratch tracks of as deposited and heat-treated Cr/CrN films on polished 1010 steel substrate. (c) As deposited CrN films with 3% N$_2$ (d) Heat-treated CrN films with 3% N$_2$. 
Fig. 4.19 Scratch tracks of as deposited and heat-treated Cr/CrN films on polished 1010 steel substrate. (e) As deposited CrN films with 5% \( \text{N}_2 \) (f) Heat-treated CrN films with 5% \( \text{N}_2 \).
Fig. 4.19 Scratch tracks of as deposited and heat-treated Cr/CrN films on polished 1010 steel substrate. (g) As deposited CrN films with 7% N₂ (h) Heat-treated CrN films with 7% N₂.
Fig. 4.20  (a) Scratch track of as deposited CrN coatings with 3% $N_2$ on 1010 steel.
Fig. 4.20  (b) Scratch track of heat-treated CrN coatings with 3% N₂ on 1010 steel.
Table VI  Critical load of as deposited and heat-treated Cr/CrN thin films on 1010 steel substrates.

<table>
<thead>
<tr>
<th>N₂ Content (vol. %)</th>
<th>Critical Load (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
</tr>
<tr>
<td>As Deposited</td>
<td>1.11</td>
</tr>
<tr>
<td>Heat-treated</td>
<td>1.18</td>
</tr>
<tr>
<td>3</td>
<td></td>
</tr>
<tr>
<td>As Deposited</td>
<td>0.8</td>
</tr>
<tr>
<td>Heat-treated</td>
<td>1.12</td>
</tr>
<tr>
<td>5</td>
<td></td>
</tr>
<tr>
<td>As Deposited</td>
<td>0.92</td>
</tr>
<tr>
<td>Heat-treated</td>
<td>1.38</td>
</tr>
<tr>
<td>7</td>
<td></td>
</tr>
<tr>
<td>As Deposited</td>
<td>1.2</td>
</tr>
<tr>
<td>Heat-treated</td>
<td>1.18</td>
</tr>
</tbody>
</table>
5. CONCLUSIONS

Pulsed DC magnetron sputter deposition of Cr/CrN films was carried out at 200°C for different nitrogen contents in the sputtering gas. This study indicates that sputter deposition is one of the candidate methods to produce hard Cr coatings. From results found in this study, the following conclusions can be obtained.

(1) Hard Cr/CrN coatings on steel substrates have been successfully prepared with sputter deposition.

(2) XRD analysis of the coatings shows that vol. % CrN in the coating increases with the increasing nitrogen content in the sputtering gas.

(3) Sputter deposited Cr coatings are nanocrystalline with the grain size being 7 – 8 nm.

(4) Microhardness measurements of pure Cr films show that higher hardness than bulk Cr due to grain size effect.

(5) With increasing nitrogen contents in the sputtering gas, the microhardness of the coated steels increases. This is due to the composite effect of CrN in Cr

(6) The adhesion property of the coatings increases with increasing nitrogen contents in the sputtering gas.

(7) Thermodynamic analysis indicates that Cr₂N is not stable at the deposition condition of this study. Experimental results also verify the non-existence of Cr₂N at 200°C. The region below 500°C of the Cr-N binary phase diagram is prepared with an eutectoid reaction occurring at 430.5°C.

(8) Rapid thermal processing (RTP) in an infrared furnace did not change the phase present in the coating since, from the XRD analysis, no extra peaks were detected after heat treatment.
(9) After heat treatment, no detectable diffusion layer was observed and no effect on hardness of coated steels was resulted.

(10) From scratch test results, the adhesion strength of Cr/CrN films on steel substrates was improved after heat treatment. Although RTP was performed at relatively low temperature and short time, RTP was the sufficient processing to increase the adhesion strength.

(11) The scratch test is one of the most sensitive techniques to find out the adhesion strength of the film. From this study, film properties such as microstructure (from XRD and SEM) and mechanical property (from microhardness) were not changed after heat treatment. However, scratch test shows the different adhesion properties of films between as deposited and heat treated specimens.
6. FUTURE WORKS

More work needs to be done in terms of characterizing the composition of the coating/substrate interface. Heat treatment at different conditions might be needed to obtain more information about effects of the rapid thermal processing. Cross sectional TEM work might be needed to provide more information about the effects of rapid thermal processing. The adhesion strength is another area that needs to be studied. The adhesion strength might be improved to introduce an interlayer such as Ti interlayer to reduce the thermal stress. A quantitative analysis of the scratch test also should be needed to provide the adhesion strength of the coating/substrate system deposited at various conditions.
7. REFERENCES


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Appendix

Hardness Measurements of Thin Films

Hardness of a material equals the mean contact pressure developed during the indentation process. During indentation the coating in the interior of the impression can only transmit the surface pressure developed by the substrate material. Any increase in measured hardness compared with that of uncoated material must originate from the coating outside the crack developed around the rim of the impression and shown in Fig. A-1.

Composite hardness can be expressed as weighted mean of the film and the substrate hardness.

\[
H_c = \frac{A_f}{A} H_f + \frac{A_s}{A} H_s \tag{1}
\]

where, \( H_c \) = measured composite hardness

\( H_f \) = film hardness

\( H_s \) = substrate hardness

\( A_f \) = the area on which the substrate mean pressure \( H_s \) acts

\( A_s \) = the area on which the substrate mean pressure \( H_s \) acts

\( A = A_f + A_s \) (Fig. A-2)

\( A_f \) and \( A_s \) can be expressed in terms of the indentation diagonal, \( d \), or indentation depth, \( D \) \( (d = 7D) \), and the film thickness, \( t \).
MODEL 1 (Soft film on hard substrate)

The film is plastically strained to match the shape of the indenter. Assuming, all the strain occur inside the volume ABC in Fig. A-3 and is extend by a flow stress $H_f$ acting over the area $A_f$. In the interior of the indentation, only the substrate is transmitted through the film. With this assumption, the increased hardness due to the presence of the film, $\Delta H$ can be
\[ \Delta H_1 = H_c - H_s \]
\[ = \frac{A_f}{A} (H_f - H_s) \quad (2) \]

\[ A_f = A - A_s \]
\[ = \left( \frac{d}{\sqrt{2}} \right)^2 - \left( \frac{d}{\sqrt{2}} - 2x \right)^2 \]
\[ = 2\sqrt{2} \sin 22^\circ \cos 22^\circ t d - 4 \sin^2 22^\circ \cos^2 22^\circ t^2 \]

where, \( x = 2t \sin 22^\circ \cos 22^\circ \)

Since \( \frac{D}{d} = \tan 22^\circ = \frac{1}{7} \)

\[ \frac{A_f}{A} = 2C_1 \frac{t}{D} - C_1^2 \left( \frac{t}{D} \right)^2 \]
\[ C_1 = \sin^2 22^\circ \]

The increased hardness, \( \Delta H_1 \), can be expressed

\[ \Delta H_1 = \left\{ 2C_1 \frac{t}{D} - C_1^2 \left( \frac{t}{D} \right)^2 \right\} (H_f - H_s) \quad (3) \]

Fig. A-3. Idealized film deformation at the rim of the impression (Model 1)

**MODEL 2** (Hard and brittle films on soft substrate)
Plastic deformation is restricted to the region AB’C in Fig. A-4. Assuming, the film accommodates the indenter by crack formation in the interior of the impression. \( \Delta H_2 \), hardness increased by the film, is expressed by

\[
\Delta H_2 = H_c - H_s \\
= \left\{ 2C_2 \frac{t}{D} - C_2^2 \left( \frac{t}{D} \right)^2 \right\} (H_f - H_s) \tag{4}
\]

where, \( C_2 = 2 \sin^2 11^\circ \)

![Fig. A-4. Idealized film deformation at the rim of the impression (Model 2)](image)

From the equation (3) or (4), the film hardness, \( H_f \), can be expressed

\[
H_f = H_s + \frac{H_c - H_s}{2C_{1,2} \frac{t}{D} - C_{1,2}^2 \left( \frac{t}{D} \right)^2} \tag{5}
\]