

PLASMA-ENHANCED DIAMOND-LIKE CARBON COATINGS ON SOFT SUBSTRATES

By

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ABSTRACT

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Diamond-like carbon (DLC) is a form of amorphous carbon that has many attractive properties such as high hardness values, chemical inertness, high electrical breakdown voltage, transparent to visible and infrared light, and strong wear-resistance. These desirable properties give DLC widespread applications. This project explores innovative DLC coatings structures and deposition technologies to address the needs for protecting soft surfaces.

An electrochemical boriding of low carbon steel and subsequent laser arc deposition of DLC were combined to create durable, low friction, low wear, and corrosion-resistant surfaces for harsh environmental conditions. The friction and wear properties of this duplex coating were studied and compared with each corresponding single layer. Finite element modeling of nanoindentation was performed to interpret the optimum thicknesses of the coatings combinations and study the mechanical properties of the duplex system. Corrosion experiments were performed to study the resistance to pinhole defects, as it is a common cause of coating delamination. Fatigue impact tests were conducted to study the resistance against indentation and crack formations. Ultimately, the duplex coating created by boride-carbon hybrid technology showed proof of the concept of low-friction, wear, impact fatigue, and corrosion-resistant in one solution.

For the first time, a single beam plasma source was demonstrated for depositing fully transparent DLC coatings at room temperature. The DLC coatings are particularly useful for protecting soft and heat-sensitive surfaces such as PET plastic.

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To my dear wife Rachael

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CHAPTER 1

INTRODUCTION

1.1 Background and Research Motivation

1.1.1 Current Carbon Coating Technology

Thin film coatings play a major role in the industries such as machining, automobile, aerospace, and electronics. A coating applied on the surface of a component acts as an interface. The main reason for applying a coating is to add a barrier against the environment. The coating inhibits specific properties for specific barrier applications, such as scratch-resistant or anti-corrosion [1,2]. Some coatings are applied to modify the surfaces. A few examples are diamond-like carbon (DLC) coatings on cutting tools for enhancing the tool lifetime, transparent conductive coatings as the electrodes for solar cells and flat panel displays, and optical anti-reflection coatings [3].

The recent research and development of coatings have emphasized the production of high-performance coatings for harsh conditions and reducing environmental pollutions [3]. For these purposes, carbon coatings have attracted great attention due to the potential of enhancing the properties and functionalities for specific applications [4,5]. There are many methods of producing carbon-based thin films and coatings. The primary methods include physical vapor deposition and chemical vapor deposition. However, the existing technologies and the resulting coatings still have many limitations.

1.1.2 Limitations of Current Coatings and Technologies

Conventional DLC coatings and deposition technologies encounter fundamental limitations, including inevitable pinholes in coatings and elevated deposition temperatures. The pinholes lead to poor chemical resistance – corrosion occurs through the pinholes, leading to the coatings delamination even though the coatings have strong mechanical properties and adhesion on the working components. An example application that requires the coatings to be able to withstand the harsh conditions of high load in a corrosive environment is the car piston cylinders. Although ta-C coatings are suitable for high wear resistance, however, the sharp change in hardness across

the interfaces and pinhole defects make the coatings unsuitable for both high wear- and corrosion-resistance.

Furthermore, there is a strong need for durable transparent coatings. A coating that can improve the wear-resistance of a soft surface such as plastic without sacrificing the optical transmittance is desirable for applications such as touch screens and vehicle headlights. Today, PECVD is the primary technology to make transparent DLCs [8]. However, the reactive species in conventional PECVD have limited energy and result in loosely packed atoms in the coatings, which limits the durability of the coatings produced at low temperatures [10-12]. Ion sources have the potential to address the fundamental limitations of conventional PECVD. Ion sources are plasma generation devices that emit ions to interact with a surface at the atomic level. There are three main types of ion sources: filament, inductive, and anode layer type. The filament type ion source uses heated filament to create ions. However, the filament can react with the gases and create unwanted radicals, which shorten the lifespan of the filament. The inductive type of ion source uses radiofrequency power to inductively generate plasma and ions [13,14]. However, the current density is low, and the ion energy has limited tunability. Anode layer ion source requires high discharge voltage, and the ion energy is usually too high for making coatings.

1.1.3 Dissertation Objective and Research

The objective of this research is to explore innovative deposition technologies and DLC-based coatings that effectively protect the soft surfaces. The objective is achieved by using computer-aided design of duplex coatings structures and developing a new single beam plasma source enhanced chemical vapor deposition. Two specific outcomes are 1) coatings for extremely harsh conditions, and 2) low-temperature-deposited transparent coatings for protecting heat-sensitive surfaces.

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CHAPTER 2

DIAMOND-LIKE CARBON AND DEPOSITION METHODS

2.1 Diamond-like Carbon

Diamond-like carbon (DLC) is a class of amorphous carbon classified by its compositions and structures, which is usually in the form of thin-film coatings. DLC coatings have many attractive properties such as high hardness values, chemical inertness, high electrical breakdown voltage, transparent to visible and infrared light, and strong wear-resistance. DLC contains both sp^2 and sp^3 hybrid bonds that have an amorphous structure. The structure can be viewed as a network of carbon atoms forming random configurations and much like a glass-like structure. DLC is classified by its composition and structure, which relates to calculating the ratio of sp^2 and sp^3 bonds by using different characterization methods [1-3]. Figure 1 shows the phase diagram of carbon and how the DLC can be categorized by its composition of sp^2 and sp^3 bonds. The DLC phase diagram shows many classifications of DLC material. For example, the tetrahedral amorphous carbon (ta-C) has high percentage of sp^3 bonds. Therefore, the ta-C has material properties that is similar to that of a diamond. But when hydrogen is introduced into the ta-C, it can be seen that the material is in the different category of hydrogenated tetrahedral amorphous carbon (ta-C:H) where the area of the material has shifted toward the hydrogen. Because of this composition difference, ta-C:H has hardness property that is lower than ta-C but has some transparency.

Carbon atoms have two electrons in both s-orbital shell and p-orbital shell. One s-orbitals and two p-orbitals bind together to form sp^2 hybrid orbitals. This results in the planar assembly of carbon atoms. A total of three sp^2 bonds are formed where two of the two σ -bonds form a 120° angle between each other, and the one π -bond is formed perpendicular to the other two σ - bonds. Graphite is an example of sp^2 hybrid structure, thus giving the name graphite-like to sp^2 hybrid bonds. This structure is made up of layers of carbon atoms with sp^2 hybrid bonds, and each layer is bonded by Van-der-Waales forces. Due to the nature of such structure, graphite is one of the softer forms of carbon [4].

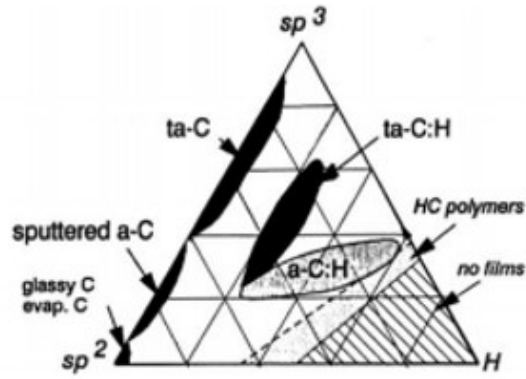


Figure 2.1: Phase diagram of DLC material [2]

Although carbon only has two electrons on its outer shell but can form bonds with four other carbon atoms. There is a very small energy barrier difference between 2s and 2p orbitals. Therefore, an electron can easily be excited from the 2s to the 2p energy state. When one of the electrons from the 2s orbital overcomes the energy potential and gets excited to the 2p orbital, a total of four hybrid sp^3 bonds are formed, with each being a σ -bond. The hybrid orbitals form a tetrahedral configuration. Diamond is purely made with sp^3 hybrid orbitals forming σ -bonds, giving the name diamond-like [4,5]. The tetrahedral structure of the carbon atoms forms a very strong three-dimensional structure, making the diamond hardest material.

DLC contains both sp^2 and sp^3 hybrid bonds that have an amorphous structure. The DLC structure can be viewed as a network of carbon atoms forming random configurations, like that of silicon in glass. Many characterization methods such as X-ray photoelectron spectroscopy (XPS) and nuclear magnetic resonance (NMR) have been used in the past to establish the structure. It is believed that the sp^3 hybrid carbon atoms form three or four membered rings, while the sp^2 hybrid carbon atoms form a cluster. The cluster of sp^2 bonds forms links between the rings of sp^3 bonds, and together they form a disordered random network.

Numerous research has revealed that the DLC consists of attractive properties such as extreme hardness, high transparency, wide redox potential range and atomically dense structure. The properties can be tuned easily by altering the material compositions, as seen in Figure 2.1. The

material can be manufactured to the desired properties to fit the application. The application of the DLC includes hard tool coatings, optical filters, moisture barriers and electrochemical electrodes.

2.2 Coating Deposition Methods

Since its first introduction in the 1970s, various forms of deposition processes have been invented and many types of DLC were developed [6]. The newly developed deposition process such as the use of plasma technology and optimizing parameters has allowed the DLC coatings to be upscaled and largely used for various applications in industries such as automotive, defense, medical, and green energy.

2.2.1 Physical Vapor Deposition

2.2.1.1 Magnetron Sputtering

In physical vapor deposition (PVD), sputtering process is a common vacuum technique used to create coatings on surfaces. A magnetron is a device that acts as a plasma source which utilizes strong electric and magnetic fields to confine energetic electrons close to the surface of the target. The strong electric field allows effective ionization of gas particles by the electrons to create plasma. The high energy ions in the plasma bombard the target material and cause the sputtering of the target atoms, which subsequently deposit on the surface of the substrate and create a layer of coating.

When a reactive gas is introduced into the magnetron sputtering process, the reactive species react with the ejected target particles. A chemical reaction occurs between two different particles to form a molecule on the surface of the substrate. This allows the deposition of ceramic, metallic alloy, or compound [11,12]. Magnetron sputtering can be easily scaled up to large-area coatings, which is preferred by the industries for manufacturing a variety of coatings.

2.2.1.2 Laser-Arc Deposition

Laser arc is a common technology used to produce hydrogen-free tetrahedral amorphous carbon (ta-C) coatings that contain high concentration of sp^3 bonds. ta-C with high sp^3 content has high hardness values close to bulk diamond. The laser arc deposition system uses a pulsed arc to evaporate the target material and produce coatings (Figure 2.2). In this process, a pulsed laser is aimed at the target where a pulsed arc is generated. The short pulse laser creates an arc on the

surface where the concentrated energy creates an arc spot. The localized high temperature in the arc spot evaporates the target material. The evaporated atoms have high energy as they deposit on the substrate, leading to excellent coatings adhesion. The target is usually designed to rotate so that another arc can be ignited by the laser at a different spot on the target [7-8]. This process is then repeated to deposit a coating of desired thickness.

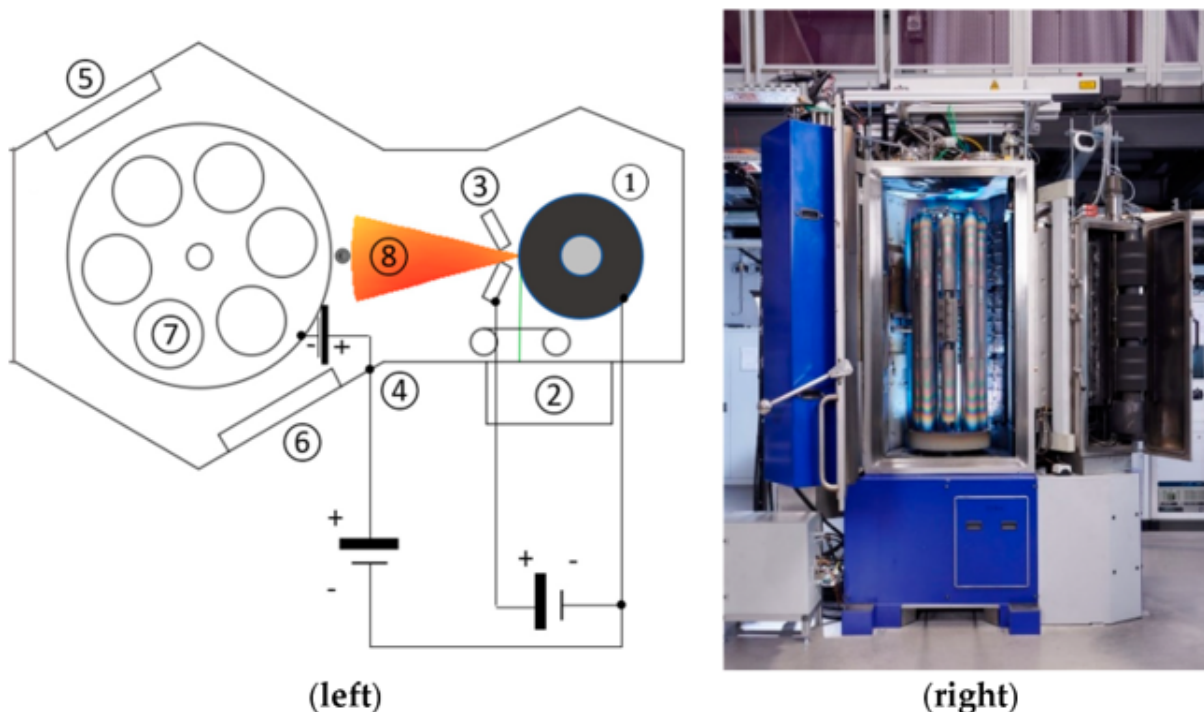


Figure 2.2: (Left): (1) cathode; (2) laser scanning system; (3) two-part anode; (4) bias supply; (5) radiation heater; (6) magnetron sputtering source; (7) substrate holder and rotation; (8) plasma (Right) Coating chamber with Laser-Arc Module™ LAM500

2.2.2 Chemical Vapor Deposition

Chemical vapor deposition (CVD) involves a chemical reaction between gaseous species and on the substrate to form a solid phase coating. This process is cheap and easy due to its ability to deposit ceramic, metal, and intermetallic compounds. It does not require a high-vacuum system like PVD to function. The process can be continuous and can be easily upscaled. The downside of CVD is toxic precursor gases are often involved, and the process usually requires high temperatures to decompose the source gases

Plasma-enhanced CVD (PECVD) uses plasma to decompose the source gas. Therefore, it can produce films at low temperatures. This process requires continuous delivery of reactive gas and a source of plasma to enable the chemical reactions [9]. The source gas (e.g., methane) is decomposed in plasma by high-energy electrons and gas ions colliding with the gas molecules. The decomposition forms reactive radicals that subsequently form carbon compounds such as graphite or DLC coatings on the substrate [10]. The process can incorporate hydrogen gas as well to make hydrogenated DLC which consists of high sp^2 content that results in highly transparent DLC, called hydrogenated amorphous carbon (a-C:H). Hence, varying the H concentration in a-C:H can result in tunable coatings properties.

2.2.3 Electrochemical Boriding Process

The boriding process has been demonstrated to harden the surface of metals to improve wear-, fatigue-, oxidation-, and corrosion-resistance [13,14]. The electrochemical boriding process is the most cost-effective method with the shortest process time. However, the process requires a high temperature, above 800°C, for molten salt [14].

In the electrochemical process, metals are immersed into the molten boride salts, such as borax and sodium carbonate [13]. Electrolysis is performed between a graphite anode and a metal sample cathode using direct current (DC). The boron is reduced and deposited on the surface of the metal. The reaction occurs between the boron and the metal surface, causing nucleation of the boron cluster. Next, the boron diffuses into the metal structure and forms a boride compound (Figure 2.3) [14,15]. The most common iron borides that form on a steel substrate are FeB and Fe_2B .

2.2.4 Ion Source Deposition

An ion source is an instrument that creates ions from a plasma source. A typical diagram of the ion source can be seen in Figure 4. Although there are many ways to ionize gas molecules, the most common method used is the electron impact process. Electrons with high energy transfer their kinetic energy to the gas molecules and ionize them. There are two ways to create electrons: one is to use a heated filament to create a thermionic effect; and the other is to use an electric potential difference between a cathode and an anode. As the electrons are accelerated, they ionize

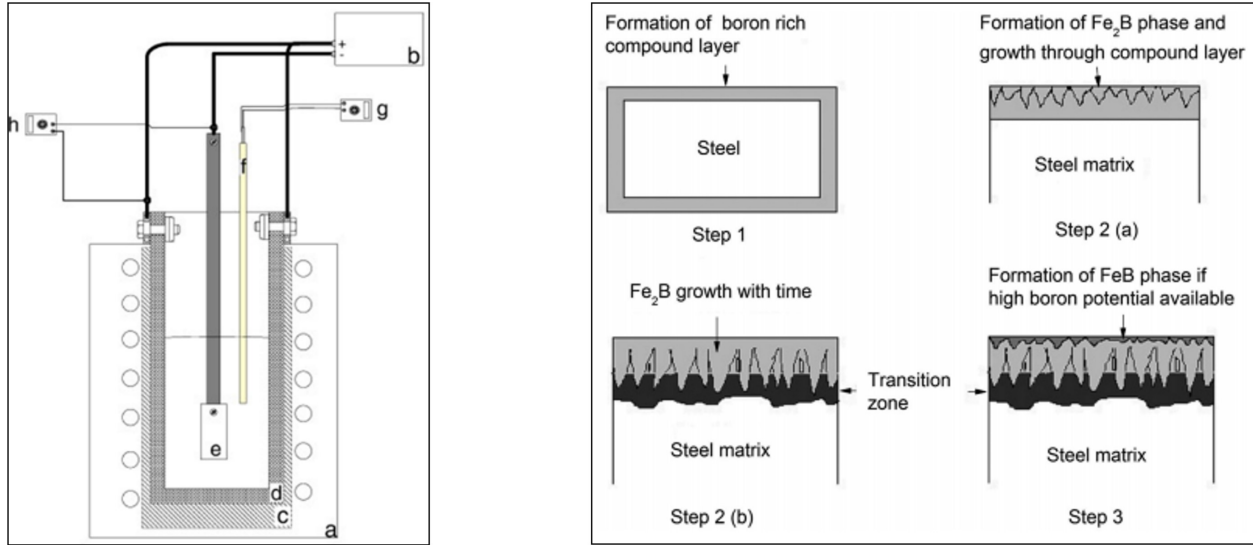


Figure 2.3: (Left): Schematic of electrochemical boriding set up, (a) furnace (b) DC source (c) alumina crucible (d) graphite crucible cathode (f) thermocouple (g) multimeter (h) multimeter [15] (Right): Schematic presentation of the mechanism of boronized layer formation on steel [16]

the gaseous molecules. The ions are attracted by the extraction electrode [17,18].

The filament type ion sources operate at a low pressure, which is incompatible with many PVD and CVD processes. In addition, the reactive gas can react and deteriorate the filament [19]. The inductive-type ion source uses RF power to generate plasma. This limits the adjustability of the ion energy and the ion current density is usually low [20]. The anode layer ion source is considered superior to the filament and inductive ion source, however, there are still limitations. The focusing of the ion beam on the substrate is limited, and a large voltage is required for the plasma discharge [19-21].

In this thesis work, a novel single beam ion source was used for depositing DLC coatings. This plasma source aims to overcome the limitations of the conventional ion sources. As shown in Figure 2.4, the single beam ion source consists of a hollow anode body with a magnet assembly surrounding the anode. The magnet generates a magnetic field parallel to the hollow anode wall and effectively confine and generate electrons to sustain plasma discharge. A positive voltage is applied to the anode and cathode. The electric field drives the ions toward the center and out of the ion source as a single beam.

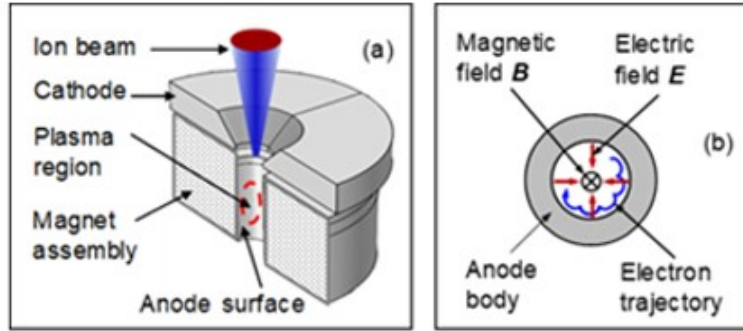


Figure 2.4: Principle of the single beam ion source. (a) Profile view. (b) Top view. (c) Two types of single beam ion sources (round beam and scalable linear beam) and discharges [25]

The discharge can be sustained at low voltage due to the strong confinement of electrons by the magnetic field. This allows a wide range of ion energy that is tunable [22-24]. Figure 2.5 shows that the discharge potential is low compared to conventional ion sources with very high voltage requirements. Also, there is a large potential drop the further away from the ion source. Therefore, the ions generated by the single beam ion source can gain high amount of energy. Therefore, by changing the applied voltage, the ion energy can be tuned.

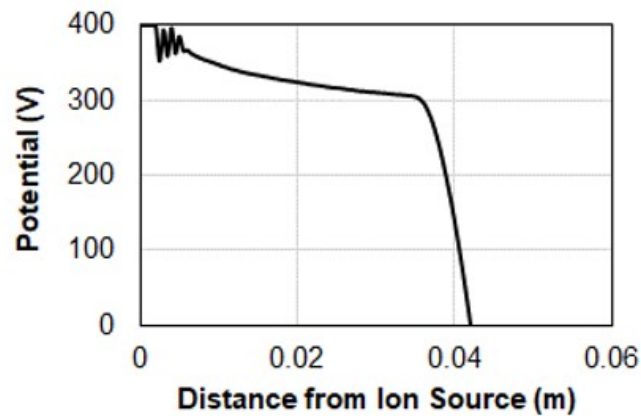


Figure 2.5: Voltage potential of ions generated by single beam ion source

2.3 Effects of Ions in Coating Deposition

Ion-source-assisted deposition incorporates ion bombardment to improve the coatings quality. There are three different ways this can be achieved. First, inert gas is used to generate non-reactive ions such as argon ions that influence the nucleation and growth of the coatings. Second, a reactive

gas such as oxygen is used to generate reactive ions that influence the growth of the coatings as well as creating a compound. Third, a gas such as oxygen or nitrogen is used to generate precursors to grow the coatings [26,27]. The schematic of ion bombardment where the mixing zone between the coating and substrate is created by high-energy ions can be seen in Figure 2.6. This zone helps to improve adhesion by reducing the sharp interface between the coating and substrate [27].

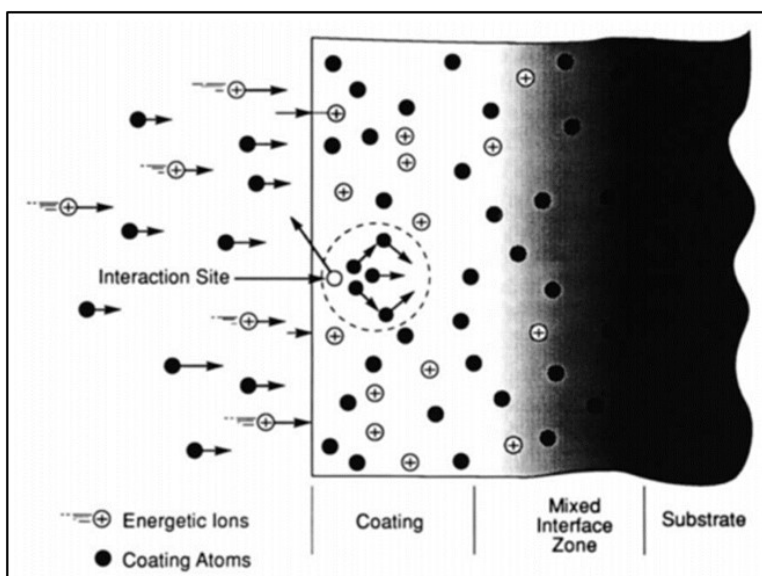


Figure 2.6: Schematic of ion beam mixing process [17]

The effect of the ions on the growth of the coating depends on the ion species, ion energy, and flux of bombarding ions. High ion energy and high ion flux are required for a high deposition rate [26]. Therefore, there is a direct relationship between ion energy and growth rates. When the coatings are grown without the ion bombardment, a long incubation period is required, during which the 'islands' of clusters form on the substrate surface. With the ion bombardment, the nucleation time is greatly shortened due to the ion-enhanced atomic mobility and nucleation sites [27].

The ion bombardment during the film growth has been shown to improve the quality of the coatings. Since the ion-atom interactions are equivalent to a localized heating, crystallization of the films can be realized even at lower temperatures below the phase equilibrium conditions. Also, it has been shown that the ion bombardment densifies the coatings as well, improving the

film quality [27]. The bombardments from high-energy ions remove any atoms with overhanging bonds and fill the voids with incoming target atoms. The ion-atom interactions also induce surface diffusion, producing a highly compact structure with low porosity [26]. It has been suggested that the ion bombardment allows the three-dimensional motion of atoms in the coatings due to the momentum transfer, where the high-energy ions transfer their kinetic energy to the coating atoms. The momentum transfer allows the atoms in the coatings to diffuse along the planes and downwards toward the substrate, which increases the packing density [17,27]. The effect of the ion beam bombardment is much more pronounced than heating the substrate.

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CHAPTER 3

DUPLEX COATING

3.1 Introduction

The objective of this project is to use DLC-based coatings for extremely harsh conditions. There is a need for wear- and corrosion-resistant coating on steel, for applications that experience high load and harsh conditions. Conventional DLC coatings and deposition technologies encounter fundamental limitations, including inevitable pinholes in the coatings and sharp interfaces.

The project focuses on creating duplex coatings with wear- and corrosion-resistance. A coating that can withstand harsh conditions of high load and corrosive environment. ta-C coatings are suitable for high wear resistance because of their super high hardness values. However, due to the sharp change in hardness across the interfaces and pinhole defects, it is unsuitable for both high wear and corrosion resistance. A duplex surface treatment will be implemented to combine the advantages of each layer. A fast electrochemical boriding process followed by a pulsed laser arc deposition will be used to produce super hard DLC coatings on top of a pinhole-free boride interlayer to address this challenge. It is hypothesized that the boride layer will prevent corrosion and add a transitional layer between the substrate and the DLC coatings. This will promote the mechanical properties and adhesion, as the elastic modulus of boride is between DLC and steel. It will allow the expansion of the application range for DLC coatings as high wear- and chemical-resistant coatings.

3.2 Previous Work

Limited studies have been conducted on boriding processes and duplex treatments. Litoria et al. [1] found that the wear behavior of pack-borided and hydrogenated amorphous carbon (a-C:H)-coated AISI 4140 steel outperformed single-treated borided specimens. The process includes very long processing times and the generation of solid waste and gaseous emissions during the commonly used pack-boriding (4–5 h of treatment time for 50 to 75 μm thick boride layers) [2-4]. However, the borided surfaces have outstanding corrosion resistance [5] and fatigue strength.

An ultra-fast electrochemical boriding process that can achieve 50 μm thick boride layers in

only 30 min is able to address the long processing time that limits the application of the process [5–7]. The existing hybrid coating technology is restricted to tribology and corrosion studies for high load bearing capacity. The studies commonly include cyclic impact tests to test the resistance of coatings under large load [8]. The cyclic load analysis the adhesion, wear and impact resistance.

A shortcoming of existing hybrid coatings is that performance measures are often restricted to tribological and corrosion studies, even though an increase in load-bearing capacity of such coated surfaces is claimed. A common way to determine the resistance of coating systems against recurring mechanical loads under application-oriented conditions is the cyclic impact test [16]. During the test, a hard, spherically shaped indenter is used to repeatedly impact a defined area of the surface layer. In between every impact, the probe is lifted off the surface. The spherical geometry loading condition results in a symmetrical Hertzian pressure distribution. As a result, critical material properties such as adhesion, wear and impact wear resistance under cyclic load can be analyzed [8–12].

Batista et al. [13] investigated the impact wear resistance of plasma-nitride and (Ti, Al)N- and CrN-coated AISI H13 steel. They showed that, compared to the single-layer physical vapor deposition (PVD) coating, substrate deformation was minimized for the duplex treated case, which resulted in less coating delamination.

Studies by Lamri et al. [14] demonstrated that the condition of the substrate influences the failure behavior of the thin film. The impact testing was conducted on CrN coatings on M2 steel in two different heat-treated conditions. They identified the presence of various types of carbides as the major reason for early failure.

Beake et al. [15,16] introduced a new setup for micro-impact and contact fatigue testing of diamond-like carbon (DLC) and TiN coatings. The probe stays in contact with the surface for the coating long duration of the test.

Zha et al. [17] developed a similar cyclic impact test scenario realizing very high frequencies of 20 kHz to mimic the load conditions during high-speed machining. They investigated monolayer TiAlSiN and multilayer TiAlN/TiSiN nanocoatings. The study showed that the edge cracked at the

tensile tests and delamination of the coating at shear stressed areas, as well as inclined cracks in the coating. Spalling areas increased with increasing impact cycles.

3.3 Finite Element Analysis Modeling

Finite Element Analysis (FEA) software ANSYS was used to model nanoindentation on the coatings system. FEA was conducted for several reasons. First, to understand the strain and stress distribution in the coatings as it is difficult to characterize complex coatings systems. Second, to determine the ideal thickness of coatings combinations. The thickness of the coatings (μm) is much thinner than the workpiece (mm). This difference imposes a challenge to efficiently model the entire system. We introduce spring elements in the FEA model, which allows us to approximate the substrate as a thin layer supported by elastic springs to enable efficient and accurate simulations.

A total of 4 different samples were modeled. 1) 1045 steel substrate 2) thick ta-C coated 1045 steel substrate 3) iron boride coated 1045 steel substrate 4) ta-c and iron boride coated 1045 steel substrate.

The stress-strain data were obtained from literature and converted into true stress and strain for the data input [18,19]. Young's modulus and Poisson's ratio from the literature were used as well. Table 3.1 shows the properties of each material. The material for the indenter was isotropic and elastic while the material for the samples was isotropic and elasto-plastic [19,20].

Table 3.1: Material properties for FEA modeling [21]

Materials	Young's Modulus (Gpa)	Poisson's ration
Diamond indenter	1140	0.04
ta-C coating	370	0.21
Boride	300	0.28
1045 AISI substrate	224	0.3

A 2-D homogenous axis-symmetric structural element type PLANE 182 was used to model the indenter and the samples for the ability of non-linear deformation. The element has nonlinear capabilities and can exhibit large strain and stress, as well as elasto-strain hardening plasticity. To model the contact, 2-D target segment TARGE 169 and contact element CONTA 171 were used on the surface of the indenter and the sample [22,23]. When the indentation occurs, the target element

can penetrate the target element's surface. To model the thick sample and minimize the substrate effect, spring elements COMBIN 14 were used on the bottom of the sample surface and vertically aligned to the constrained nodes [24]. The element allows us to decrease the thickness of the steel substrate without eliminating the effect of the bulk. By incorporating the COMBIN 14 element, a small bulk of the material can be modeled, which saves the computation time while increasing the accuracy of the nanoindentation.

To identify the correct spring element properties, nanoindentation with different stiffness of spring elements was conducted and Young's modulus was calculated from the resulting load-displacement graph. Once the stiffness corresponding to the correct Young's modulus of the substrate was identified, nanoindentation with different indentation depths was conducted.

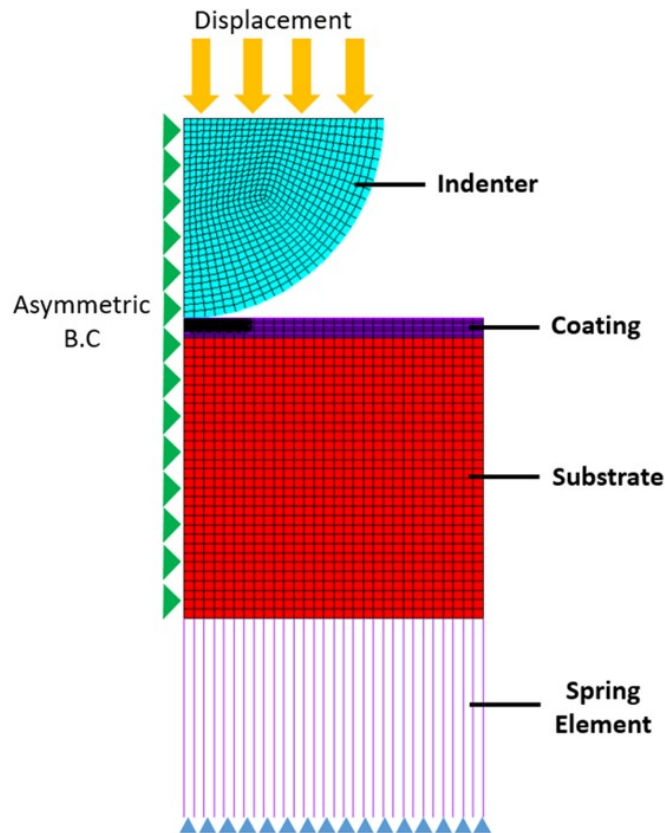


Figure 3.1: 2D asymmetric FEA model of nanoindentation with spring elements

The geometry of the models was constructed and meshed (Figure 3.1). To save computing time, an asymmetric plane was assumed and only half of the indenter and sample geometry was

constructed with the tip of the indenter [22,23]. The geometry of the spherical indenter tip was modeled as a sphere. The identified and calculated spring element was implemented in all the FEA models (Figure 3.2).

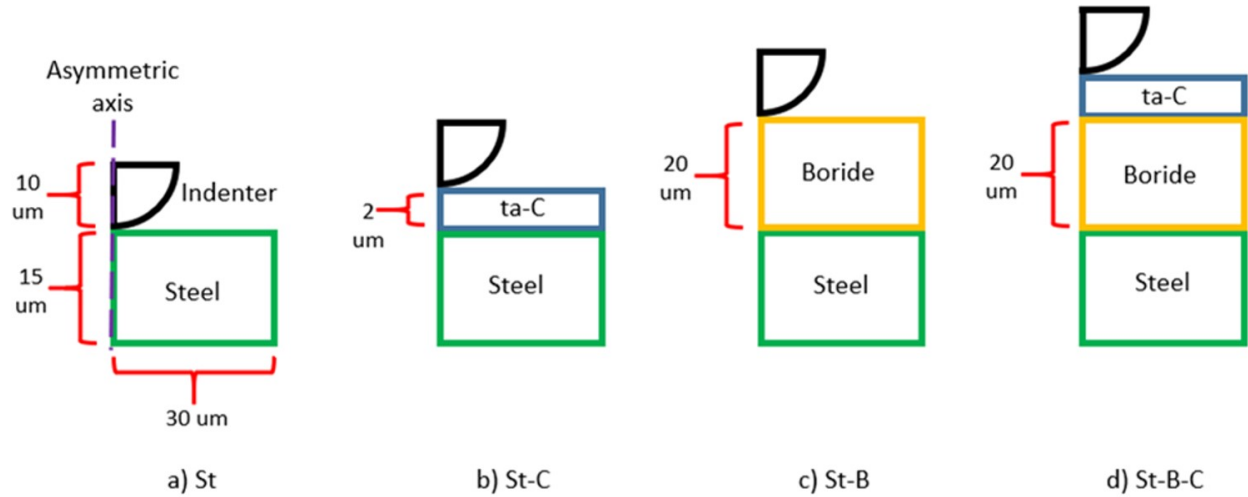


Figure 3.2: FEA geometry of samples a) Steel substrate (St) b) ta-C coated steel (St-C) c) Boride coated steel (St-B) d) ta-C and boride coated steel (St-B-C) [21]

Two different sets of studies of nanoindentation were conducted. In the first study, a consistent force was applied on top of the indenter for all the samples. In the second study, the depth of the indentation was kept at a constant value for all the samples while the force was varied. The correct depth and the force were calculated by applying different depths and forces on the St model. The depth and force when the steel experienced the plastic deformation were recorded.

First, the ideal spring stiffness was calculated by conducting multiple nanoindentations of 200 nm depth with different spring stiffness property input on the St FEA model. A load - displacement curve was generated from the nanoindentation simulations. From the curve, Young's modulus was calculated. The values of Young's modulus at different spring stiffness can be seen in Table 3.2. It showed that the spring with 1×10^5 stiffness resulted in the closest Young's modulus to the substrate.

The measurements of Young's modulus at different indentation depths was measured to ensure the accuracy of the spring element, which can be seen in Table 3.3. The Young's modulus found was determined acceptable due to variation under 10%. The Young's modulus at 200 nm indentation

Table 3.2: Spring stiffness and Young's modulus of St sample

Spring Stiffness (N/m)	Young's Modulus (Gpa)
$5 * 10^4$	260
$1 * 10^5$	226
$3 * 10^5$	300
$1 * 10^6$	245

depth was closest to Young's modulus of the steel which was 224 GPa.

Table 3.3: Indentation depth of indenter and calculated Young's modulus

Indentation Depth (nm)	Young's Modulus (Gpa)
80	195
100	206
200	226
500	245

The ideal thickness of boride was identified by examining the stress distribution in the coating during indentation. The thickness of the boride had to withstand the force of the indentation and prevent the stress from deforming the substrate.

A force of 1.2 mN and a 14 nm indenter depth were identified as the indentation force and depth which was where the substrate started to experience the plastic deformation. Different models of St-B were made with different thicknesses of boride coating: 5, 10, 20, and 40 μm to examine the effect the boride layer has on preventing the deformation of the steel substrate. The stress distribution in the y-axis of the samples which is under the indentation tip can be seen in Figure 3.3. It showed that thickness difference did not affect stress distribution. The stress curves were all same, which meant that a 5 μm thick boride layer was enough to prevent the plastic deformation of the substrate.

The resulting indentation depth with 1.2 mN of force applied on the indenter can be seen in Figure 3.4. The smallest depth from the indenter was found to be St-B-C (14.31 nm), which was expected due to the high hardness of ta-C and a thick layer of boride. Also, the depth of St-B (15.14 nm) and St-B-C were comparable while still being less than St-C (16.34 nm) which showed the

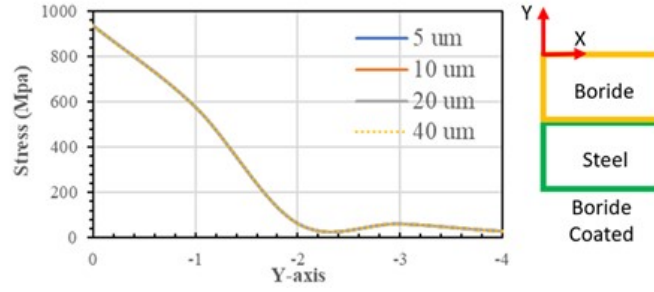


Figure 3.3: Stress distribution of boride coating at different thicknesses [44]

importance of the boride layer for increasing the resistance to deformation.

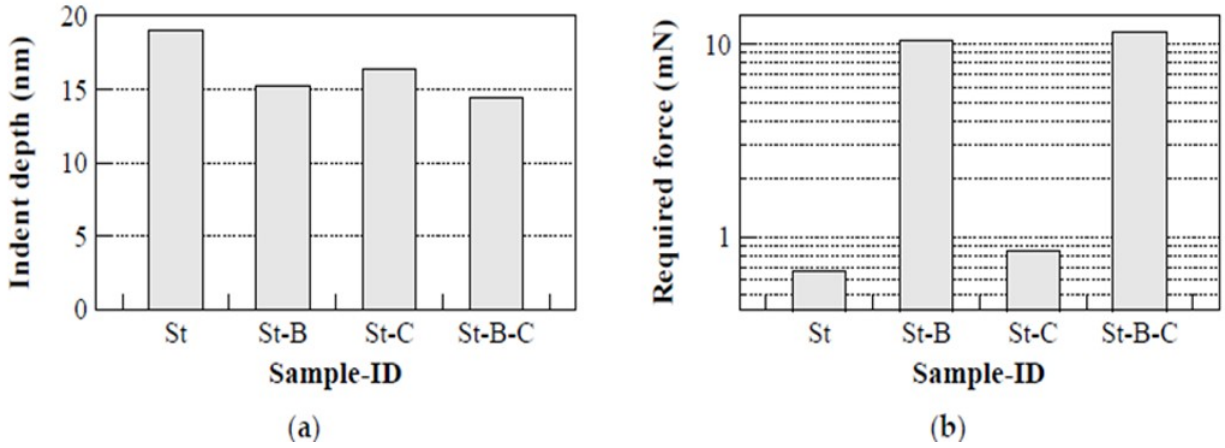


Figure 3.4: FEA modeling of nanoindentation for (a) constant force applied on the indenter (b) constant depth of indenter and resulting force [21]

The forces required to push the indenter to a depth of 14 nm were varied throughout the samples. The St (0.6637 mN) and St-C (0.8464 mN) samples required much less force than the St-B (10.43 mN) and St-B-C (11.97 mN) samples which showed that the softer steel substrate was the limiting factor in resistance to deformation. The St-B-C sample required more force (11 mN) than the St-C sample due to the thinner ta-C coating layer.

The stress distribution on the coating under the tip of the indenter was analyzed to observe the behavior of the coating under the indenter depth of 14 nm and indenter force of 1.2 mN. The stress distribution in the y-axis of the samples which is under the indentation tip with constant applied force on the indenter and constant depth of the indenter can be seen in Figure 10. The St-B-C

sample exhibited the highest stress (2424.8 MPa), followed by St-C (1708.3 MPa) and St-B (521.03 MPa). It showed the importance of ta-C and boride coating as St-B-C and St-C samples consist of the same material on the top, the stress distributes into the sample as far as 1 μm . Without the boride sample, the stress is enough to plastically deform the steel substrate. But with the boride layer, the sample can withstand the high stress as it is not high enough to plastically deform the boride layer. The visual stress distribution of the FEA model under the indentation can be seen in Figure 3.6.

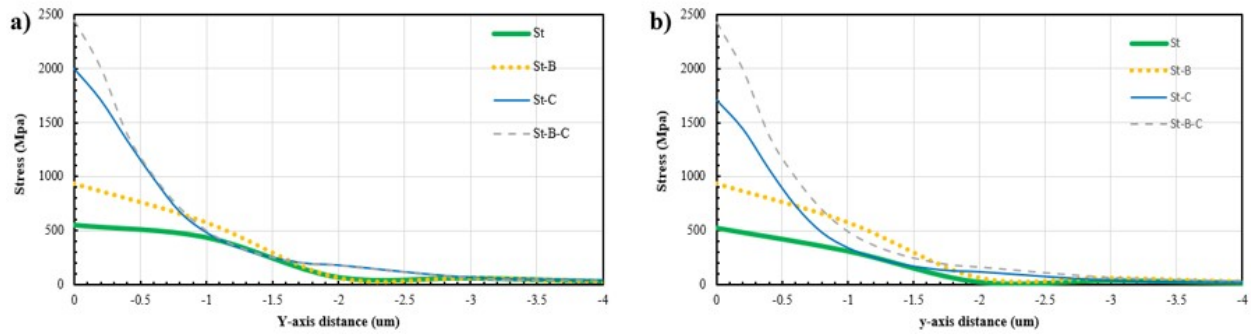


Figure 3.5: FEA modeling of nanoindentation for a) constant force applied b) constant depth of indenter and resulting stress distribution on the coatings

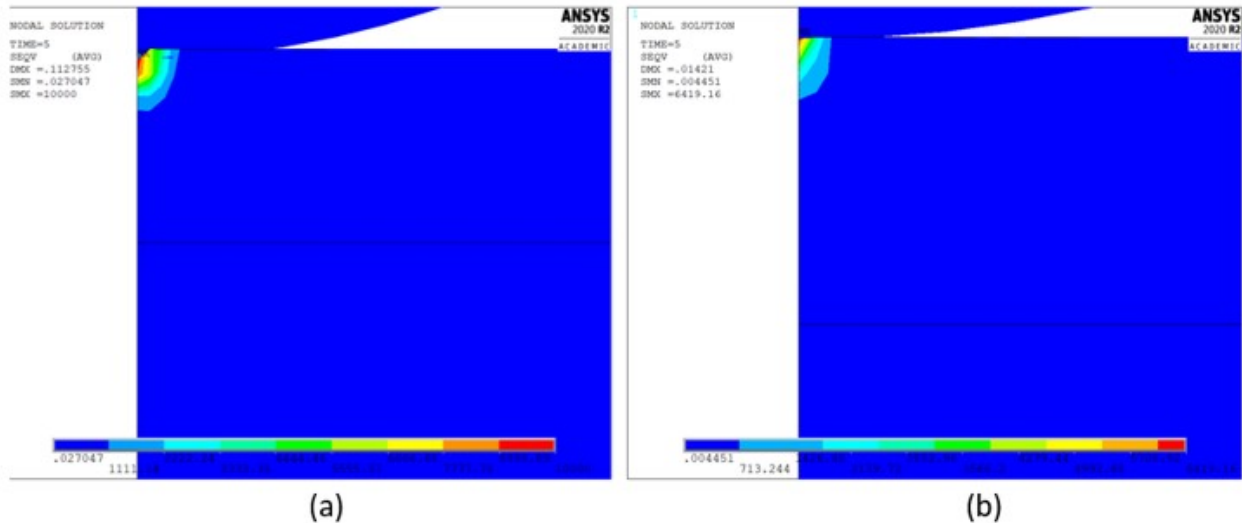


Figure 3.6: FEA model of Von-Mises stress distribution of (a) St-C sample at a constant depth of indenter (b) constant force applied on the indenter

From the FEA calculations, the ideal thickness of each of the coatings were calculated. For the

top ta-C coating, $> 2\mu\text{m}$ was suggested while for boride layer, $> 20\mu\text{m}$ thickness was suggested. It should be noted that from previous calculations, there were no big differences between 5 and $20\mu\text{m}$ in terms of mechanical properties. However, the uniformity of the boride layer is unclear and for practical reasons, $20\mu\text{m}$ was suggested to ensure that the boride layer covered the entirety of the steel substrate.

3.4 Experimental Verification – Fraunhofer Tests

The surface of a disk-shaped AISI 1045 low carbon steel was polished and ultrasonically cleaned. The iron boride coating was produced using the electrochemical boriding method. The coating was conducted in 90% borax and 10% sodium carbonate molten salt bath at 950°C temperature with 18.4 A current and 1.3 V voltage for 20 minutes [25,26].

The samples were cleaned in boiling deionized water and polished to remove any unwanted surface residues [21]. The ta-C coating was produced using the laser pulse controlled cathodic arc evaporation method to promote the formation and stabilizations of sp^3 bonds in DLC coatings. To ensure proper adhesion of ta-C with the substrate, a layer of Cr/C interlayer was produced with a thickness of 200 nm using the direct current cathodic arc method [27,28]. The sample was polished and cleaned once again. Using these methods, three samples were created. St-B (Boride coated steel), St-C (ta-C coated steel), and St-B-C (both boride and ta-C coated steel).

Table 3.4: Sample ID and summary of coatings on samples [21]

Sample-ID	AISI 1045 Steel	Boride	Ta-C Coating
St-B	x	x	
St-C	x		x
St-B-C	x	x	x

3.4.1 Thickness Measurements

The boride coating thickness was measured through optical microscopy of a cross-section of the sample. Ten locations of the highest points were measured and averaged. The ta-C coating thickness was measured using the calotte grinding method and optical microscopy while the boride layer was measured through optical microscopy of cross-sectioned samples.

The cross-sections of the St-C and the St-B-C samples can be seen in Figure 12. The thicknesses of the ta-C coating and the boride layer were 2 μm and 58 μm , respectively, which were the sufficient coating thicknesses that were determined previously by FEA. The boride layer showed ‘teeth’. The thickness was determined by measuring the heights of valleys and peaks of the ‘teeth’ at ten locations and averaging the thickness. The high temperature of the boriding process caused the microstructure of the steel to change. The steel substrate showed coarser-grained microstructure and the hardness was measured. The steel substrate hardness of the St-C sample was 236 HV0.1 while the St-B-C sample was 265 HV0.1. The change in hardness showed the attribute of substrate microstructure change from the boriding high temperature process [25,26,27].

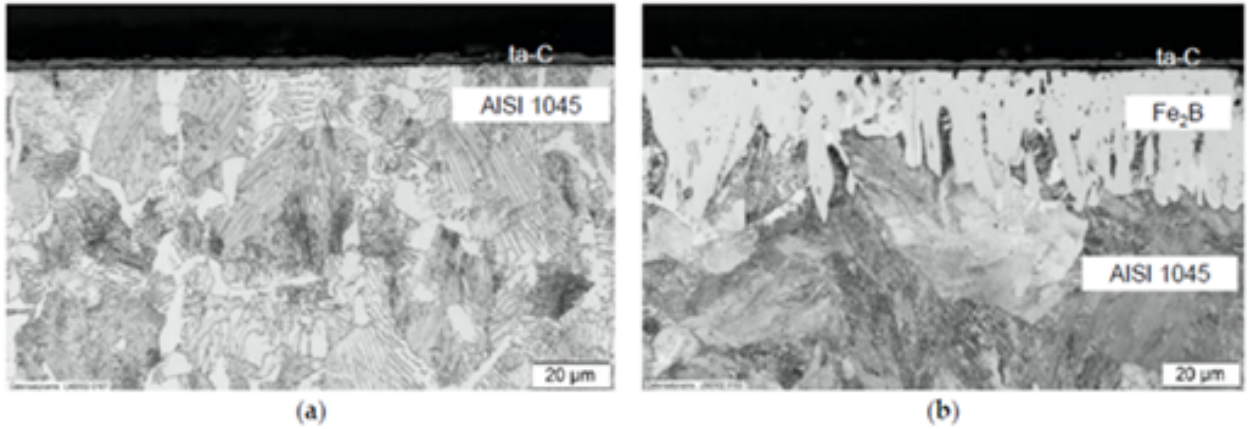


Figure 3.7: Cross-section of sample (a) St-C and (b) St-B-C [44]

3.4.2 Wear Rate / Coefficient of Friction

To measure the wear rate and coefficient of friction of the samples, a reciprocating 440C stainless steel ball on disk set up was used. A total of 12,500 cycles were conducted on the St-B and St-B-C samples. The sliding rate of the ball was 2 cm/s on an 8mm track which the total distance traveled was 100 m. A pressure of 5 N was applied on the ball which resulted in 1 GPa Hertzian contact pressure [21]. The wear rate can be calculated using the equation below:

$$k = \text{wear volume}(\text{mm}^3) / \text{load}(\text{N}) * \text{sliding distance}(\text{m}) \quad (3.1)$$

The coefficient of friction (CoF) for the St-B-C sample proved to be much lower than the St-B

sample. From Figure 3.8, the CoF of the St-B-C sample was 0.14 while the St-B sample was 1.19, showing a much higher value. The ST-B-C sample showed little traces of the track left from the steel ball, but the St-B sample left a significant trace showing wear from the run. The wear tracks and the depth of the tracks can be seen in Figure 3.8. The St-B sample had a depth of $7.8\ \mu\text{m}$ with a wear rate of $6 \times 10^8\text{mm}^3\text{N}^{-1}\text{m}^{-1}$ while the St-B-C sample had almost no depth of $0.18\ \mu\text{m}$ with a rate of $5 \times 10^5\text{mm}^3\text{N}^{-1}\text{m}^{-1}$.

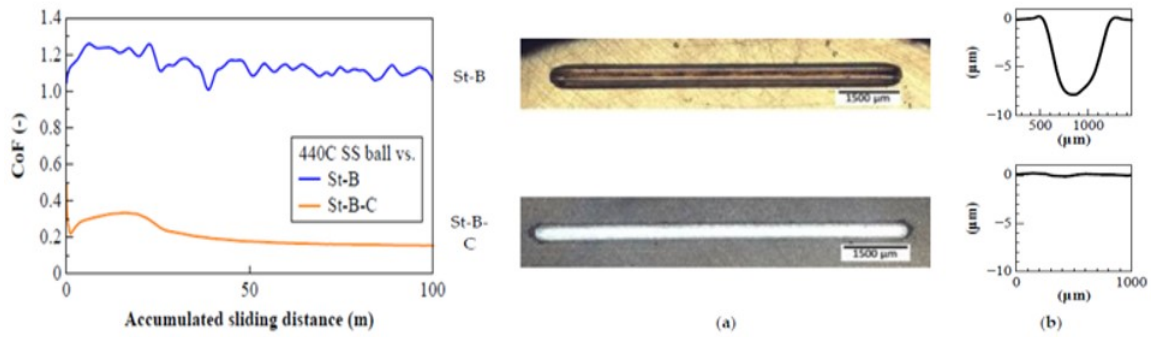


Figure 3.8: Coefficient of friction as a function of sliding distance under dry conditions and (a) Optical microscope images and (b) sample wear tracks for St-B and St-B-C [21]

3.4.3 Impact Tests

Impact testing was conducted to assess the surface's dynamic load-bearing capability of the St-C and St-B-C samples using a servo-hydraulic test bench Instron 8501 and custom set up. The indentation was applied vertically onto the surface of the samples via a compression die and a spherical probe of tungsten carbide. A force of 100 N was used with frequency at 10 and 20 Hz [29,30]. With the custom set up, a total of 12 impact tests were conducted using different levels of forces; 1,2,3, and 4 kN with three different load cycles; 1,1000 and 100000 [21]. The impact sites were examined after the tests. Cross-sections were made to examine the microstructure and integrity of the coatings.

The impact spot diameters were measured for both St-C and St-B-C samples. By increasing the load and the cycle number, the diameter of the spot also increased for both samples. The increase of the load had more effect on the diameter size than the cycle number. A trend can be seen in Figure 3.9 that the diameter size of the St-C sample was larger than the St-B-C sample which agreed with

the results from the FEA model.

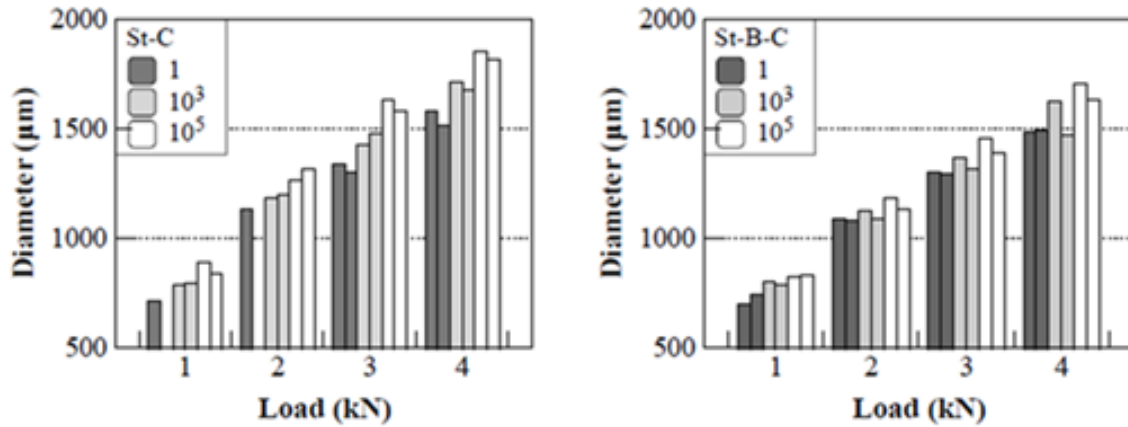


Figure 3.9: Impact diameter of (a) St-C and (b) St-B-C sample at different load cycles as a function of different loads (1,10,3105) [21]

The cycle 1 and cycle 10⁵ samples were analyzed with the SEM to evaluate the damage to the coatings. From the SEM pictures in Figure 14, the St-C sample did not show any cracks under the 2 kN load, but a small crack can be seen at the 3 kN load. Increasing the load and cycle number resulted in greater crack lengths. At 4 kN and 10⁵ cycles, the coating experienced significant damage. Long cracks in tangential directions could be found and cracks in the radial direction and multiple spalling regions were found at the outer impact region (Figure 3.10).

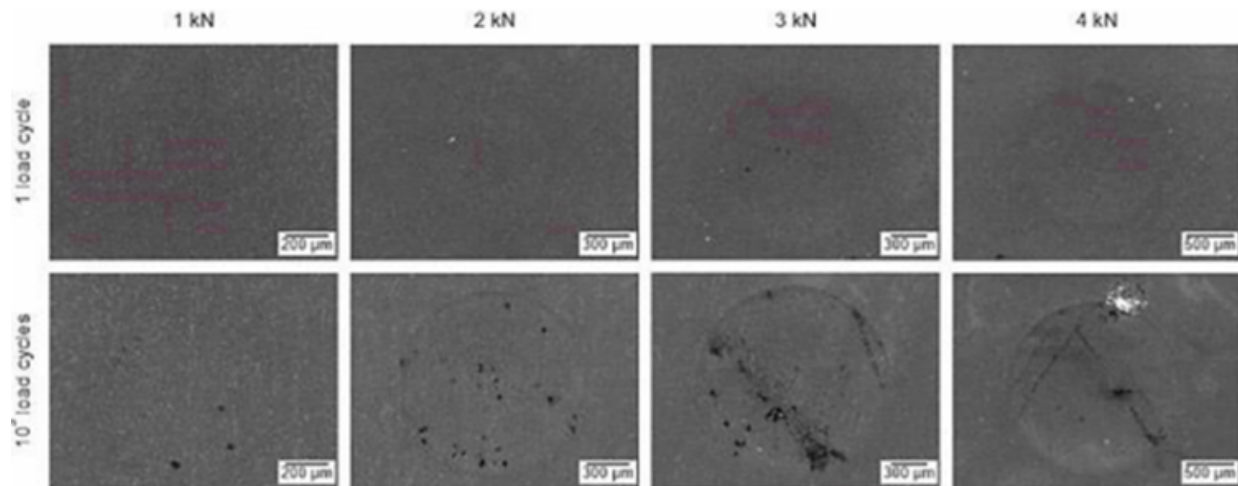


Figure 3.10: SEM images of impact sites of St-C samples at various loads and cycles of indentation [21]

The SEM pictures and small cracks were found on the St-B-C sample after 2 kN load and 103 cycles can be seen in Figure 15. When compared to the St-C sample, the damage to the coatings was more intense and 105 cycles intense as the load and cycles increased. The indentation marks become clearer and cracks along the edges of the indenter marks can be seen. Tangentially oriented cracks in the impact area were found, as well as radial cracks at the outer edge of pile-up.

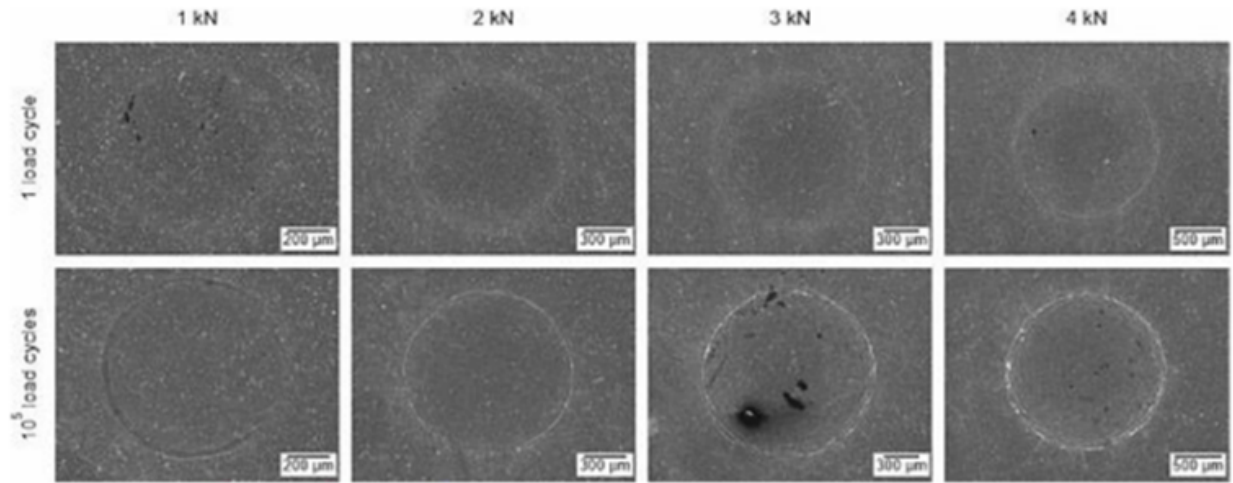


Figure 3.11: SEM images of impact sites of St-B-C samples at various loads and cycles of indentation [21]

The impact testing showed the differences in the mechanical behaviors of the coating samples St-C and St-B-C. Higher resistance to indentation of St-B-C sample compared to St-C sample can be seen in Figure 16 with smaller and less defined indentation marks. The high hardness of the boride coating relieved the stress from the ta-C coating. Also, the high-temperature boride process altered the microstructure of the steel substrate and increased the hardness of the substrate which additionally contributed to the impact resistance. Since the St-C sample was able to tolerate a higher load compared to the St-B-C sample, it can be suggested that the cracks initiated at the boride coating or the interface between the ta-C and boride coatings. It can also be suggested that the boride process left surface defects and internal irregularities in the boride layer which led to stress concentration areas and crack initiation zones.

3.4.4 Corrosive Environment Test

Corrosion tests were conducted on St-C and St-B-C samples to study the resistance to pinhole corrosion. The samples were submerged in 15% hydrochloric acid for 3 hours at room temperature [21]. After the submersion, the surface morphology and elemental composition were analyzed in JEOL JSM-6610 Series SEM.

The corrosion test on the St-C and St-B-C samples resulted in delamination of the ta-C coatings for both samples. It was assumed that the boride layer in the St-B-C sample would withstand the corrosion and prevent the delamination by preventing any pinhole defects [31,32]. This result suggests that the delamination occurred at the interface between the boride and Cr/C coating layer. To validate this, a new sample without the Cr/C layer was produced; St-C-noCr and St-B-C-noCr.

The SEM image from Figure 3.12 shows the St-C-noCr sample pinhole defects. Delamination of the coating from the pinhole corrosion can be seen in Figure 3.13 as well. The St-B-C-noCr sample showed no delamination after the test which confirmed the previous suggestion. The SEM images from Figure 18 did not show any pinhole defects. The surface composition and morphology showed only a little difference. The results from the corrosion tests showed that the boride layer was able to protect the substrate from any pinhole corrosions and keep the ta-C coating intact without the Cr/C coating layer. The boride layer was able to prevent the formation of pinhole defects and delamination of ta-C coatings as hypothesized [33-35].

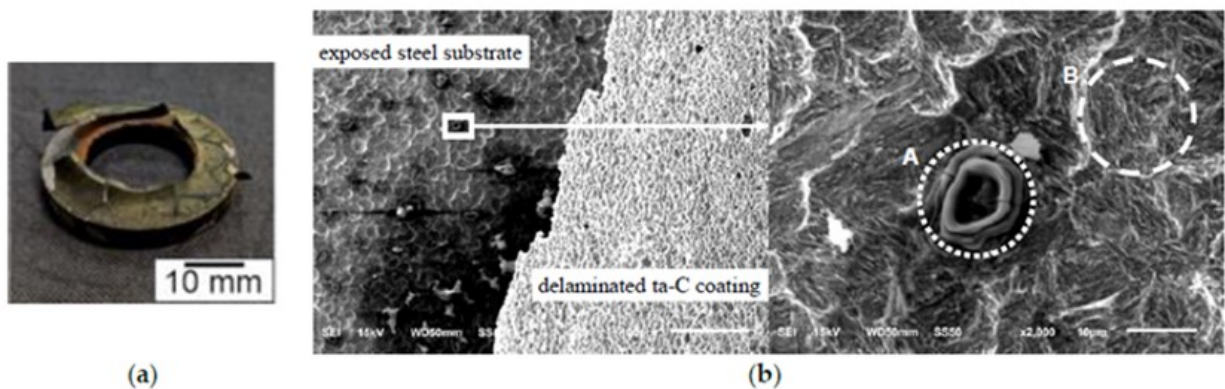


Figure 3.12: St-C-no Cr sample (a) sample after the corrosion test (b) SEM image after corrosion test. A corrosion pin can be observed. [21]

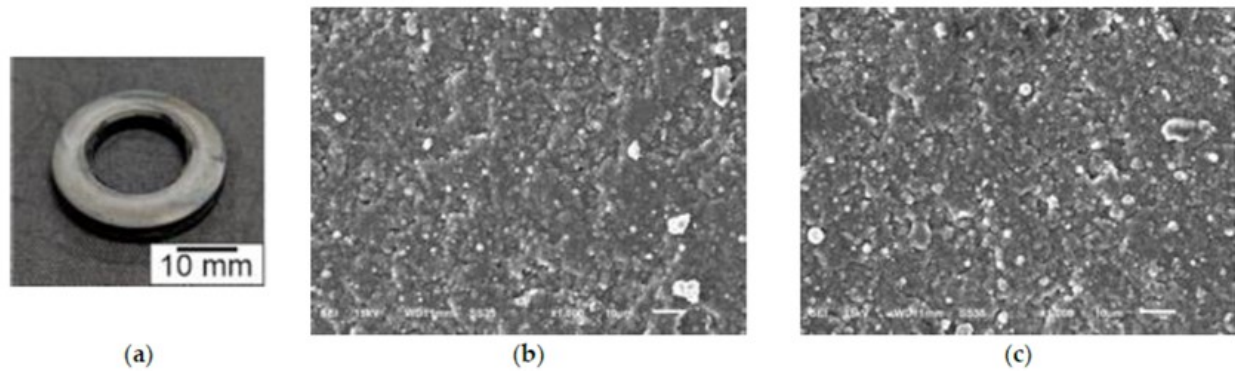


Figure 3.13: St-B-C-no Cr sample (a) sample after the corrosion test (b) surface morphology before corrosion test (c) surface morphology after the corrosion test [21]

3.5 Conclusion

The FEA model was able to predict the ideal combination of duplex coating thicknesses. The St-B-C sample consists of laser pulse-controlled cathodic arc evaporation deposited ta-C on top of electrochemically borided AISI 1045 low carbon steel with a Cr interlayer. The sample showed promising overall performance in mechanical strength and corrosion resistance compared to St-C and St-B samples.

The coefficient of friction comparison showed that the St-B-C sample had the lowest value. The impact test results agreed with the FEA modeling and showed that the St-B-C sample had the highest resistance to the impact load and plastic deformation. The boride layer was able to provide support for the ta-C coating, but it showed that the coating tended to crack. Under the corrosion study environment, the ta-C coating tended to delaminate but unlike the cause of delamination of the ta-C coating in the St-c sample, the cause was not from pinhole defects but the dissolution of the Cr interlayer. The corrosion resistance of the St-B-C sample improved when the interlayer was removed.

The study showed that boride-carbon hybrid coating technology can be used in application as a low friction, wear, impact fatigue, and corrosion-resistant coating. Further study of the ta-C coating under high cyclic load needs to be conducted and further investigation on boride and ta-C interface needs to be performed as well.

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REFERENCES

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CHAPTER 4

MAGNETRON SPUTTERING & ION SOURCE ENHANCED DLC COATINGS

4.1 Introduction

Amorphous carbon (a-C) coatings have many attractive properties such as high hardness, low friction, low roughness, and high resistivity [1-3]. By adding hydrogen to form hydrogenated amorphous carbon (a-C:H), the coatings become softer but more transparent than a-C [4]. Therefore, a-C:H is particularly suitable for applications where highly transparent and moderate wear-resistant coatings are needed. Examples of applications include moisture barrier and wear-resistant coatings for perovskite solar cells, plastic packaging materials such as PET and parylene, and touch screens.

Hydrogenated amorphous carbon coatings have been produced by physical vapor deposition (PVD), chemical vapor deposition (CVD), and plasma-enhanced chemical vapor deposition (PECVD) [1,4,5]. PVD involves vaporization of coating material with plasma source in order to create a coating. The technique offers several advantages such as improving the substrate material properties, ability to organic material as coating, and is considered relatively fast. However, the technique lacks in ability to coat complex shapes, high processing cost and complexity of the process itself.

Ion sources are plasma generation devices that enable ion beams to interact with the materials at the atomic level as they are deposited to effectively modulate the film microstructure [6]. Two major types of ion sources have been widely used for thin-film processing – gridded and end-Hall ion sources [12,13]. The gridded ion source has a relatively low current and high ion energy (e.g., >300 eV), which usually leads to large stress and graphitization of the carbon films. Gridless end-Hall ion sources can produce ions with a wide range of average energy (e.g., 40-200 eV) at a much higher current than gridded ion sources. These characteristics are beneficial for the high-rate deposition of dense a-C:H films. The requirement for a closed-loop drift of the electrons in end-Hall ion sources leads to circular or racetrack beam patterns, while some applications would demand the ions be focused onto a specific area. Furthermore, end-Hall ion sources have a narrow ion-emitting slit,

which could be coated quickly, resulting in unstable discharges [7-11].

This study shows the deposition of highly transparent and durable DLC thin films. The transparency is high enough to be transparent through visible light, and the durability is high to prevent the soft plastic substrate from scratches. The deposition uses magnetron and single beam ion source to modulate the material process and coatings properties and address the need for durable transparent coatings. A coating that can improve the wear resistance of a soft surface such as plastic without sacrificing the optical transmittance is highly desirable for applications such as touch screens and vehicle headlights. This study is conducted in three steps. First, depositing DLC films with RF reactive magnetron sputtering. This is a common method to make coatings. Second, using a newly developed single beam ion source to confirm its capability to enhance PECVD of DLC coatings. Finally, combining the magnetron and ion source to modulate the DLC properties. The effects and benefits of the ion beam on the coating's properties are showed.

4.2 Previous Work

Many deposition methods have been proven to create DLC coatings. Most of the past studies aimed to achieve a specific property of amorphous carbon coatings, such as high hardness [16,17]. The mechanical properties seem to be the focus of the material. The Young's modulus of the material is commonly measured by nano-indentation methods and analyzing the load-displacement curves. The most reported elastic modulus of amorphous carbon (a-C) coatings ranges from 100 GPa to 180 GPa. [37-45] The modulus value seems to drop when hydrogen is incorporated during the process to produce hydrogenated amorphous carbon (a-C:H). the elastic modulus. Methods such as magnetron, cathodic arc, pulsed laser and microwave plasma are the most common methods used to deposit the coatings with elastic modulus that ranged the typical value [37-41]. The cathodic arc and pulsed laser method showed the ability to create coating with the highest elastic modulus of 300 GPa [37,38]. However, the studies did not show the optical properties of the coating. It did not mention the optical properties or said that the application of the coating was not optical and strictly mechanical.

In recent years, the carbon-based coating has attracted interest for applications other than

mechanical, such as optical. Although, there are many studies done, the report on the optical properties is extremely limited because the mechanical properties are still favored. A study by Seker, Z. et al [44] showed the highest transmittance value of DLC coating using microwave plasma method. However, the study did not show added mechanical properties such as elastic modulus or hardness. It was difficult to find studies that reported on both mechanical and optical properties. Some studies such as Ankit, K et al [46] did report on both properties. However, the optical properties were poor with the highest transmittance value at 60% and elastic modulus of 120 GPa. The common optical bandgap of the a-C:H coatings reported were 2.0 eV [47-50]. It was difficult to find studies where both bandgap and mechanical properties were reported. This shows the research gap to bridge the optical and mechanical properties of DLC coatings. The reported either only report on one property or when they do report both, it lacks the desirable value.

Many deposition methods have been developed with inventions of new devices. Ion sources have been an interest for its simplicity and versatility. Ma, W.J. et al [51] reported on making DLC coating with newly invented ion source device. However, no properties of the coatings were reported. Kim, WangRyeol et al [52] reported on DLC coating with ion source as well. But the study only reported on the hardness value of 50 GPa and slow deposition rates. The many ion source devices were one of a kind that was manufactured for the specific research group. Many devices were designed complicated and showed minimal data of the coating properties [51-54]. Markwitz, A et al [53] used ion source beam to produce DLC coating with high elastic modulus at low temperature. The coating was very smooth and had elastic modulus of 160 GPa. However, the deposition required extremely high voltage of 2.5kV as well a high voltage bias on the substrate. The reported optical properties were transmittance percentage of 80% at visible light wavelength.

Anita, V et al [55] was able to produce DLC using PECVD method using magnetron reactive sputtering method. They were able to achieve remarkably high deposition rate using pure methane gas. But the process required extremely high RF power, up to 400W. A bias voltage on the substrate was also applied, up to 800V. They did not report on the coating properties other than its hardness, however.

Producing highly transparent a-C:H with high density and hardness is a challenge to conventional PECVD [20-23]. The limitation arises from the plasma characteristic of PECVD, in which the chemical species are not under thermal equilibrium [16]. This means the average electron energy (e.g., 3 eV) is much higher than the ions (e.g., 0.07 eV) and the neutral species (e.g., 0.03 eV). Therefore, the ions and neutral species have little kinetic energy as they reach the substrate. It has been demonstrated that applying a negative bias to the substrate can effectively densify the a-C:H by attracting the positively charged ions to bombard the growing film [24]. Although applying a negative bias could be difficult in some applications such as coatings on a plastic sheet in a continuous roll-to-roll process, this idea has inspired the use of ion source to deposit transparent a-C:H coatings with high Young's modulus.

4.3 Plasma Discharge Characteristics

Conventional magnetron sputtering methods uses direct current (DC) power. However, DC power sputtering results in DLC with an opaque coating. In order to produce DLC with high optical properties, study was conducted between DC and RF (radio frequency) power argon plasma discharge using computation simulations.

Figure 4.1 shows the electric potential of plasma discharges by the magnetron. The magnetron is positioned at the bottom while the substrate is positioned at the top. The target surface in contact with the bulk plasma is often called the 'racetrack' area because this area is subjected to the strongest ion bombardment in conventional DC magnetron discharge, creating a racetrack groove on the target surface. This racetrack area is also the effective target area for collecting current in DC magnetron discharge, which is generally about one order of magnitude smaller than the total area of the target surface [56]. For RF magnetron discharge, once the discharge reaches a periodic steady state, the density and profile of the bulk plasma are basically stable, with small changes in one RF period.

RF magnetron discharge showed that the charge accumulation on the dielectric target surface is expected but is not uniform, due to the above-mentioned nonuniform electron flux. Positive argon ions are accumulated below the bulk plasma region, where the electrons are locally confined by the

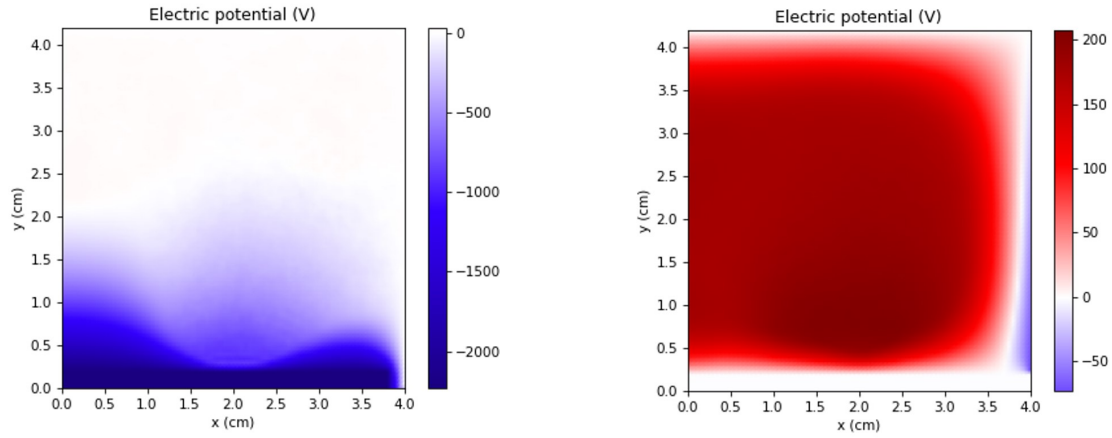


Figure 4.1: Electric potential of argon (Left) DC plasma discharge and (Right) RF plasma discharge via magnetron [56]

transverse magnetic field and cannot reach the target surface. This nonuniform surface charging results in a perturbation of the potential distribution on the dielectric target surface with a similar profile. This in turn significantly affects the ion energy distribution function (IEDF) of the ions reaching the dielectric target surface. The IEDF is spatially dependent along the dielectric target surface. RF magnetron discharge shows that the ion energy at which the IEDF peaks at different locations on the dielectric target surface varies, approximately corresponding to the difference in potential from the highest time-averaged potential to each location. Although the maximum plasma density appears near the racetrack region, the ion energy is low. On the other hand, the ion energy gradually increases beyond the racetrack region, resulting in a relatively uniform energy distribution for all the ions bombarding the dielectric target surface, as shown in the right marginal plot. The distortion of the electric potential distribution caused by the nonuniform charge accumulation has an impact on the electron dynamics, which can be clearly observed from the electric field distribution [56]. It was theorized that by using the RF power, during the deposition, the ion bombardments to the coating would be sufficient to encourage hydrogen ions incorporation to the coatings that would produce high quality transparent DLC.

4.4 Deposition Method

4.4.1 Reactive Magnetron Sputtering

The depositions were performed in a customer-made vacuum system with a load lock. A single beam ion source (SPR-10, Scion Plasma LLC) and a magnetron (Kurt J. Lesker) were used as the plasma source. The distance from the substrate to the plasma devices were set at 38 mm. The process gas was methane (10%) with argon (90%). A graphite target (99.999% C) was used for the magnetron. The base pressure for the deposition was $<8 * 10^{-4}$ Pa. The deposition pressure was 1.6 Pa. The deposition was performed on $25 \times 25 \text{ mm}^2$ glass and Si wafer substrates at room temperature. The substrates were ultrasonically cleaned in acetone and methanol in sequence, each for 15 minutes. Then the substrates were dried using compressed nitrogen gas and placed in an oven at 80°C for 30 minutes

The magnetron was excited by RF power of 13.56 MHz and the power used was 40 W. The deposition time was adjusted to achieve 100 nm thick coating.

4.4.2 Ion Source Deposition

A single beam ion source (SPR-10, Scion Plasma LLC) was used as the plasma source. It consists of an anode with a center cavity and a closed bottom. The anode opening is 12 mm in diameter. A cathode cover is located above the anode. A magnet assembly generates a magnetic field that forms a closed loop inside the anode cavity to confine the electrons. Details of this single beam plasma source can be found in reference [25]

4.4.3 Ion Source Enhanced Magnetron Sputtering

Both plasma device, single beam ion source (SPR-10, Scion Plasma LLC) and a magnetron (Kurt J. Lesker) were used for the deposition (Dual Set-up Deposition). Same conditions were used for the deposition as before, with same preparation of the samples. The base pressure for the deposition was $<8 * 10^{-4}$ Pa. The deposition pressure was 1.6 Pa with methane (10%) with argon (90%) gas.

The RF power for magnetron was set at 40W while the RF power of ion source was also set at 40W. The deposition time was adjusted to achieve coating of 100 nm thickness.

4.5 Characterization Method

4.5.1 Thickness Measurements

The thickness of the DLC coatings was measured using the Dektak XT profilometer system step function with a silica tip. A mask was used to create a step between the substrate and the coating to measure the thickness. The tip was dragged along the surface for 1.5 μm , crossing the masked area halfway. The thickness was measured three times on three different locations and averaged.

4.5.2 Transmittance and Reflectance Measurements

The optical transmittance and reflectance of the coatings were measured by a spectrophotometer (F20, Filmetrics) and a clean glass slide was used as a baseline for comparison. The background was measured by blocking the detectors while the light source was turned on. A light source was shined on the sample. The detector above the sample measured the reflectance, while the detector at the bottom measured the transmittance. The transmittance and reflectance percentage were measured at different light wavelengths and plotted to analyze the transmittance of the coating.

4.5.3 Young's Modulus and density

A laser acoustic surface wave spectroscopy instrument (LAWave, Fraunhofer) was used to measure the elastic properties and density of the coatings. The LAWave system measures the properties by non-destructive method using surface acoustic waves created by short laser pulses. The system detects the acoustic waves at a certain distance and calculates the wave propagation velocity of the surface acoustic wave. By inputting the propagation velocity, Poisson ratio, and thickness, Young's modulus and density can be calculated.

The system creates a dispersion curve, which is a plot of frequency of the pulse laser versus propagation velocity. With the increase of the frequency, the propagation velocity increases as well. The acoustic wave propagates mostly in the coating as the penetration depth is reduced. The curve is dependent on the elastic modulus of the material, as the system performs a curve fitting on the measured curve to measure Young's modulus of the coating. [35,36]

4.5.4 Surface Morphology

The surface morphology was measured by atomic force microscopy (AFM Hitachi AFM 5100N). A 5 μm tall pyramid shape Si tip was used with 20 nm radius cantilever. The scan was conducted on the middle area of the sample where the coating was thickest. Tapping mode was used to keep constant separation and force between the tip and the surface. A three-dimensional morphology of the sample surface was created.

4.5.5 X-ray photoelectron spectroscopy

The material composition was measured by X-ray photoelectron spectroscopy (XPS) system (Perkin Elmer Phi 5600 EXCA) with magnesium K_{α} X-ray source. Atomic composition of the coating surface was determined as well as the percentage of sp^2 and sp^3 carbon hybrid bonds. The peaks of the spectrum were fitted using Gaussian function. The peak areas of each element were identified and narrowed down the peaks for sp^2 and sp^3 bonds. The peak area was divided by the sensitivity factor to determine the quantitative information.

4.6 Results and Discussion

Figure 4.2 shows a typical plasma discharge image of the single beam ion source. The a-C:H coatings were deposited at different RF power. With the 40 W RF power, the deposition rate was 5.17 nm/min. The young's modulus was 29 GPa and density was 1.79 g/cm³. The mechanical values were extremely low compared to other DLC coating reported in other studies. The reaction between the target and gas molecules occurs on the surfaces. Even if a compound is formed in the gas phase, it is believed that the kinetic energy of the compound molecules cannot be easily dissipate, so the compound dissociation occurs. Therefore, the deposition rate is slow, and the ions do not have enough energy to form DLC coating with high elastic modules.

The RF powered reactive sputtering DLC was analyzed first. Figure 4.3 shows that when RF power was used, instead of conventional DC power, the coating was fully transparent with low absorption from visible to infrared (IR) spectrum. However, when the coating's mechanical properties were measured, it revealed that the coating was soft (Table 4.1).

It was concluded that the magnetron sputtering did not generate enough energy for the ions to

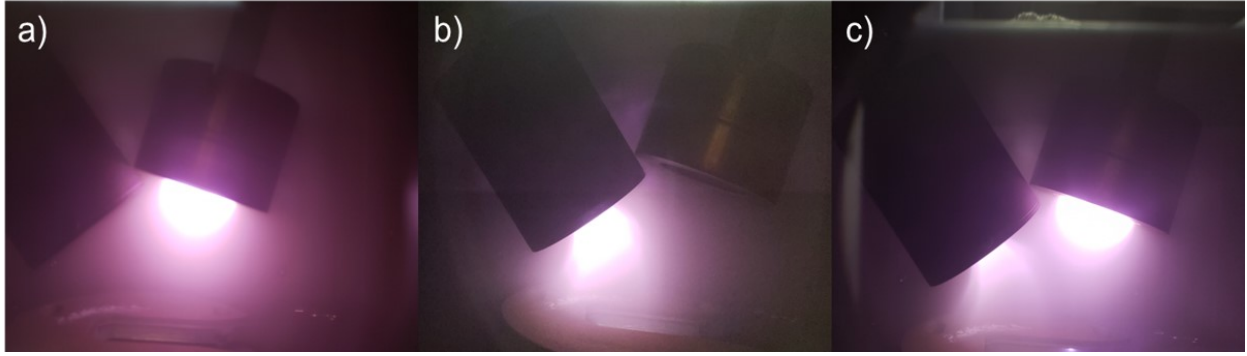


Figure 4.2: Plasma discharge image of a) magnetron, b) single beam ion source, c) dual set up

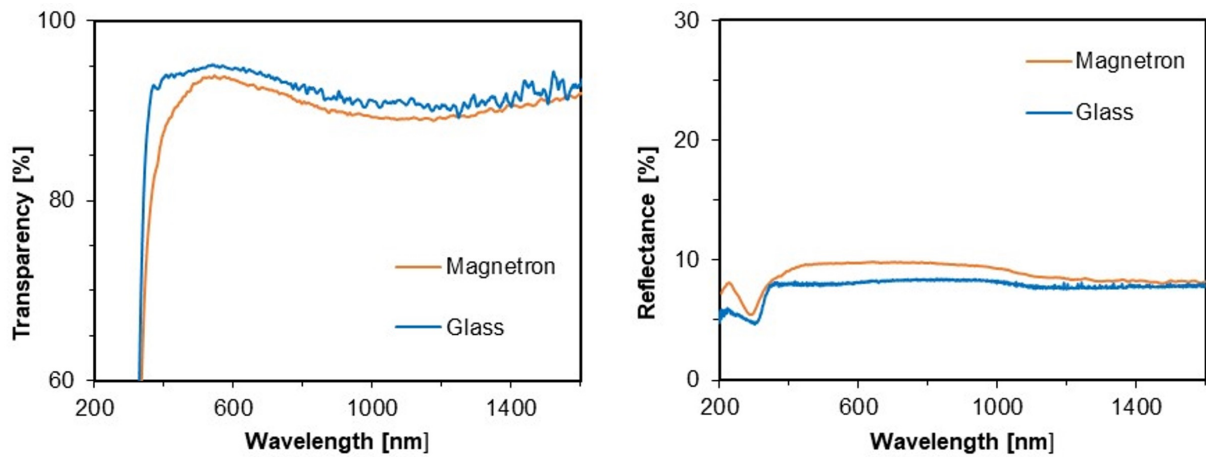


Figure 4.3: (Left) Transmittance and (Right) reflectance spectra of the a-C:H coatings produced by the RF power reactive magnetron sputtering

Table 4.1: Mechanical properties of reactive spoutering DLC

Method	Young's Modulus (Gpa)	Density (g/cm^3)
Magnetron Sputtering	29	1.79

produce hard DLC coatings. This was confirmed when the coating's composition was analyzed by XPS (Figure 4.4). Table 4.2 shows that sputtering method generated very low percentage of sp^3 content, which explains the low mechanical properties of the coating.

Table 4.2: Summary of carbon bond percentage for magnetron sputtering methods

	sp^2 (%)	sp^3 (%)
Magnetron	7.69	16.55

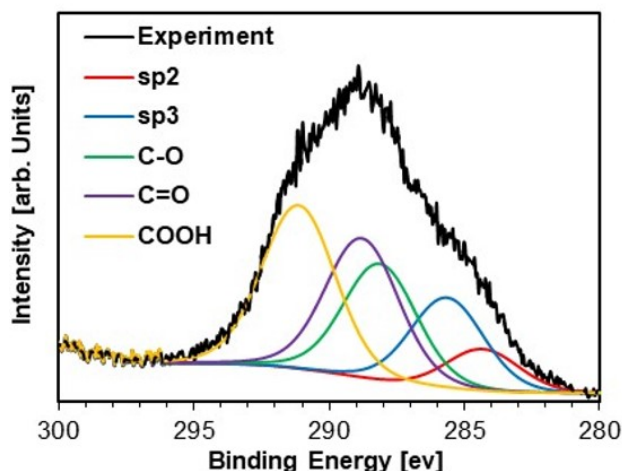


Figure 4.4: XPS spectrum of magnetron deposition with fitted curves of atomic bonds

Due to the reactive magnetron sputtering producing weak coating, PECVD process with single beam ion source method was investigated. Figure 4.5 shows the film deposition rate dependence on the power. The deposition rates were deduced from the film thicknesses and deposition times. The deposition rates increased almost linearly with the RF power because a higher RF power resulted in higher plasma density. It is worth noting that the ion energy was proportional to the RF power. If the RF power was too high, film delamination could occur due to the large ion energy. Under each power, the deposition time was adjusted according to the deposition rate to produce films of 100 nm thickness. Figure 4.6 shows an example of the coating thickness profile on a glass substrate measured with the profilometer. It confirms the film thickness was 100 nm.

Table 4.3 summarizes Young's modulus and film density of the a-C:H coatings. Although the film density nearly did not change, the modulus was lower at 40 W RF power compared to the other films. A decrease in Young's modulus is usually an indication of hydrogen incorporation. It is known that ion energy is proportional to the RF power. Therefore, energetic ion bombardments enhanced hydrogen incorporation in the film.

The mechanical properties of the DLC produced by the PECVD method produced better quality coating than the reactive sputtering method. The slight decrease in the young's modulus at higher power occurred. At higher energy, the high kinetic ion energy caused some coating materials to be

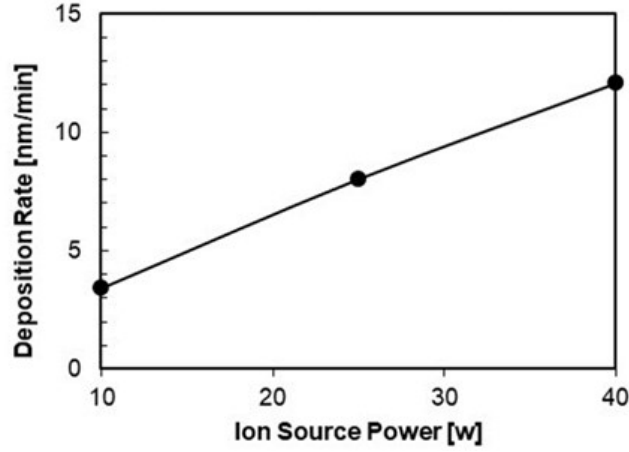


Figure 4.5: Deposition rate dependence on the ion source RF power

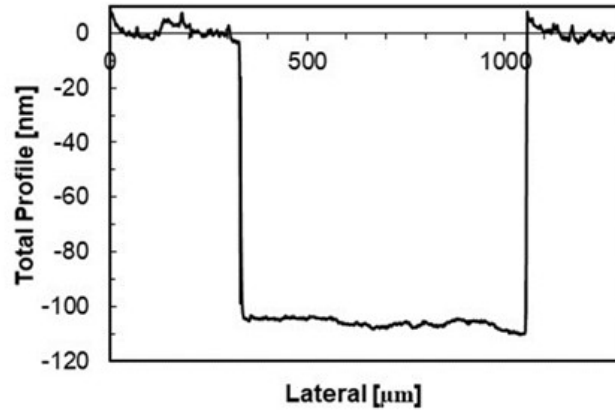


Figure 4.6: Surface profile of the a-C:H coating on a glass substrate

Table 4.3: Summary of mechanical properties of a-C:H coating by ion source deposition method

Power (W)	Young's Modulus (GPa)	Density (g/cm^3)
10	76	1.92
25	75	1.91
40	70	1.9

ejected from the substrate surface after the formation. The high ion energy might have caused higher implantation of hydrogen ions into the coating. This effect might have contributed to weakening of the coating's properties.

The optical properties of the coatings were investigated. Figure 4.7 shows the optical trans-

mittance and reflectance spectra of the a-C:H coatings with a thickness of approximately 100 nm. The films were highly transparent, and the transmittance was over 90% in the visible light range and is close to 90% even in the short wavelength range down to the absorption limit of the glass substrate (380 nm). Overall, the transmittance spectra of the coatings prepared with different RF powers were similar. There was a slight increase in the transmittance around 400 nm wavelength as the deposition RF power was increased to 40 W. This result is consistent with Young's modulus data – the coatings included more hydrogen content at higher deposition power and became more transparent. The reflectance spectra of the coatings deposited at different RF powers were also similar. There is a slight increase in the reflectance in the short wavelength range as the power increases. From the transmittance and reflectance spectra, the absorption coefficients of the a-C:H coatings could be deduced.

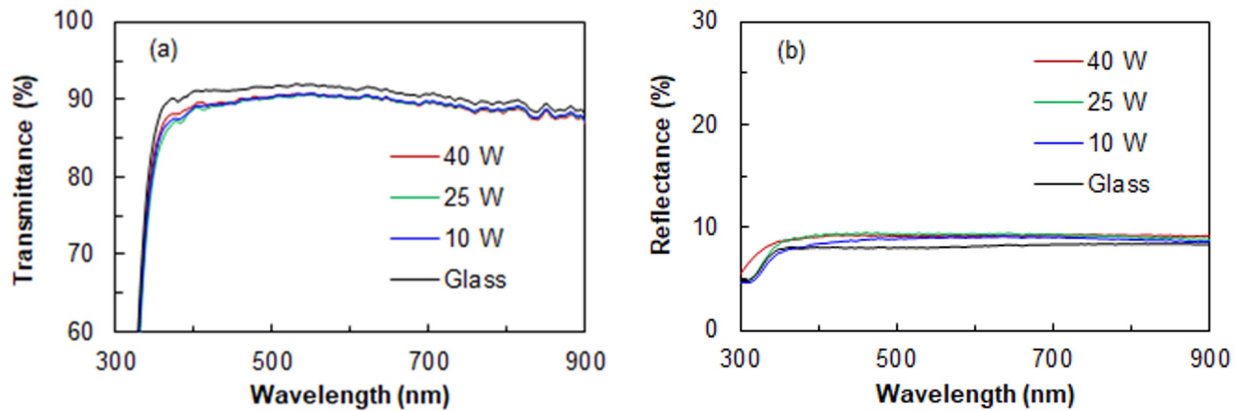


Figure 4.7: . a) Transmittance and (b) reflectance spectra of the a-C:H coatings produced by the ion source at different RF power

The optical band gap of the coatings was calculated from the transmittance (T) and reflectance (R) data, from which the absorption coefficient (α) was calculated using the following equation.

$$\alpha = 1/t * \ln(1 - R/T) \quad (4.1)$$

where it is the thickness of the coating. The optical band gap values were estimated from the Tauc plot shown in Figure 23. The predicted optical band gap was around 3.7 eV. The deposition power had little effect on the optical band gap of the coatings. The value was above what typical

carbon-based coating shows. The higher band gap indicates that the ion source deposition method produces a coating with higher transmittance and allows the transmittance of higher energy light waves.

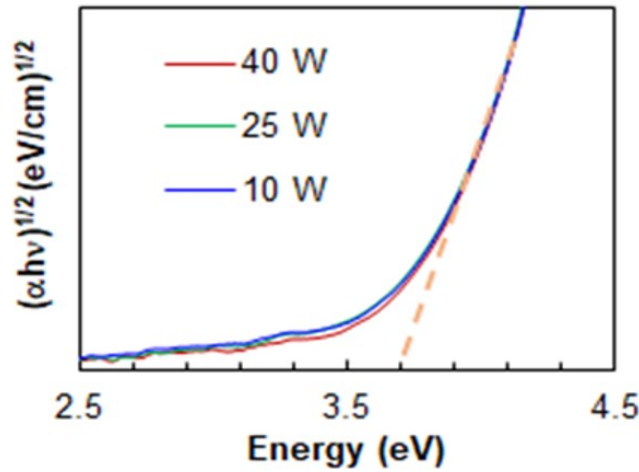


Figure 4.8: Tauc plot of the a-C:H coatings produced at different ion source power

Atomic force microscopy (AFM) was performed in an area of $2\ \mu\text{m} \times 2\ \mu\text{m}$ on the samples deposited on the polished Si substrates. Figure 24 shows the 3D images of the coatings produced at different power. Table 6 summarizes the root-mean-square roughness. All the coatings exhibited similar roughness values.

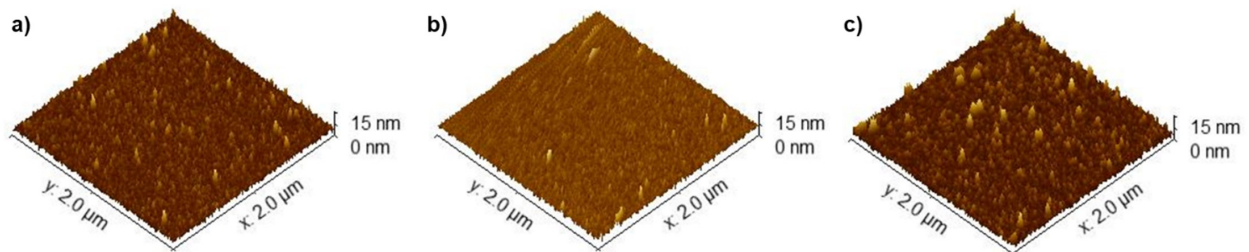


Figure 4.9: AFM images of a-C:H coatings on Si substrate with deposition power of a) 40 W, b) 25 W, and c) 10

The dual set-up deposition was conducted to evaluate the effects the ion source has on the magnetron sputtering process. The dual set-up deposition showed the highest deposition rate. This shows that the sputtering magnetron method produces small amount of hydrocarbon radicals to form

Table 4.4: Surface roughness of a-C:H coatings deposited with different ion source power

Power (W)	s_q (mm)
10	1.187
25	1.104
40	1.126

the a-C coating than by ion source method. The ion source method also produces carbon molecules with higher energy, which results in higher deposition rates. By combining both magnetron and ion source, the deposition rate is the highest because it produces the largest amount of carbon radicals for the coating material on the substrate.

Figure 4.10 shows the deposition rate of each deposition methods. The ion source deposition rate was higher than the reactive magnetron method. The dual deposition method does indeed have the highest deposition rate. The value of the rate near the value of the ion source and magnetron rates combined.

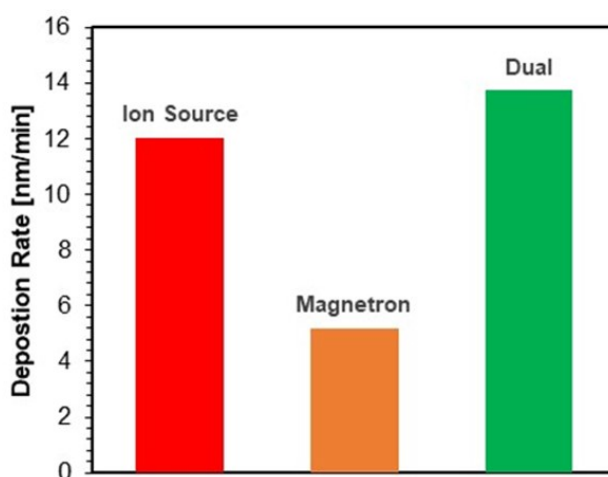


Figure 4.10: Deposition rate of magnetron, ion source and dual set-up deposition methods

Table 4.5 summarizes Young's modulus and film density of the a-C coatings. The magnetron method produced a-C with the lowest mechanical properties with the lowest elastic modulus and density. Ion source produced the highest mechanical properties, while the dual set up method a-C material had mechanical properties between the magnetron and ion source method. This further

proves that the ion source method produces carbon radicals and ions with higher energy than the magnetron. It was speculated that when combining the two methods together, the ions and radicals loses the energy due to recombination and collision occurs more frequently, which results in the ions losing its energy.

Table 4.5: Summary of mechanical properties of a-C coating

Method	Young's Modulus (GPa)	Density (g/cm^3)
Magnetron	29	1.79
Ion Source	77	1.92
Dual	39	1.82

Figure 4.11 shows the optical properties of the a-C coating with approximately 100 nm thickness. The coating appeared to be highly transparent. The transmittance was over 90% in the visible light range and short wavelength as well. Although the magnetron showed a light higher transmittance than the ion source, the difference was not significant. The dual method showed a decrease in the transmittance compared to other methods, but the transmittance was still above 90% in the visible light range. The reflectance spectra of the coatings were similar. There was a small decrease in the spectra for the dual method at smaller wavelength (<350nm).

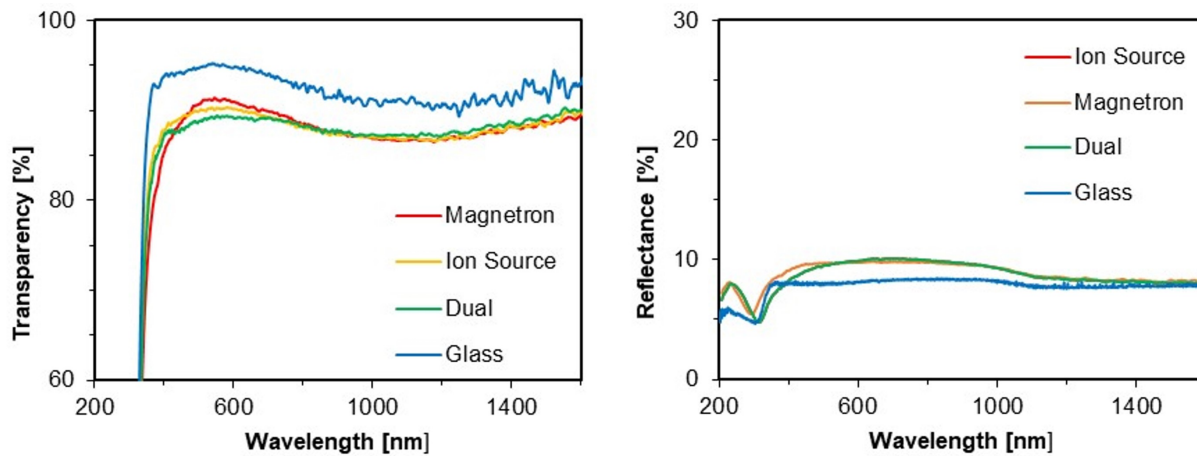


Figure 4.11: (Left) Transmittance and (Right) reflectance of the a-C coating

The optical data correlates with the mechanical properties. The magnetron showed the lowest mechanical properties and slightly higher optical properties. The sputtering method proved to

produce a weak coating because the method was not able to generate carbon ions with high energy, which results in weak carbon coating with characteristics more like graphite. However, the method proved that magnetron with reactive gas method can be used to create a-C coating instead of using graphite target and insert gas.

XPS was conducted on the samples of three deposition methods. DLC material properties comes from its material composition that is like diamond and graphite. sp^2 and sp^3 percentage was calculated to relate the material properties and composition that results from different processing methods. Figure 27 shows the XPS spectrum with fitted sp^2 and sp^3 curves. Other elements were detected, but for this research, only carbon bonds were the focus.

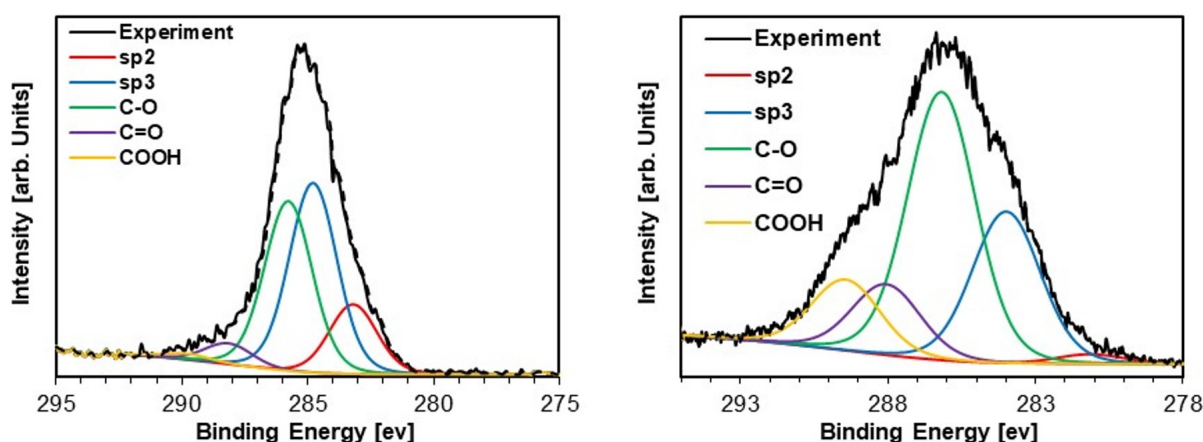


Figure 4.12: XPS spectrum of (Left) ion source and (Right) dual deposition method with fitted curves of atomic bonds

Table 4.6: Summary of carbon bond percentage for different deposition methods

	sp^2 (%)	sp^3 (%)
Magnetron	7.69	16.55
Ion Source	15.38	41.62
Dual	1.72	26.47

The ion source deposition methods show the highest sp^3 percentage. The material composition correlates with the material properties. The ion source deposition coating exhibited the highest Young's modulus, which can be related to material composition that is closer to that of a diamond. Magnetron deposition method resulted on coating with the weakest properties. The coating also

has the lowest percentage of sp^3 carbon bonds. The dual deposition method that has the mechanical properties that is between magnetron and ion source deposition, it also has the sp^3 percentage that is between magnetron and ion source deposition method. The mechanical properties of the coatings correlate with the XPS results. However, the XPS data does not seem to explain the high optical properties such as high transmittance and optical band gap. The optical properties do not seem to be affected by the sp^2 and sp^3 content.

However, the data has showed that the material property is tunable by adjusting the material properties. DLC coating that is weak to hard can be produced without having to sacrifice the transparency. This opens up more opportunity for the material, as it can be used to decrease the sharp interface challenges. DLC coating can be produced with increasing mechanical properties gradually. The gradual increase of mechanical properties would decrease the formation of sharp interfaces and decrease the likelihood of coating delamination. The solution would be very similar to the implantation of boride coating in the 'Duple Coating' research.

4.7 Conclusion

PECVD method with newly developed ion source was able to produce a-C coating with high mechanical and optical properties. The method produced ions with higher energy and created a denser coating than the magnetron method. The higher ions were able to densify the carbon coating material on the substrate and create a stronger coating. The dual method proved to fabricate coating with properties between magnetron and ion source method. However, by combining the two plasma sources together, the deposition rate was able to increase without sacrificing the optical properties significantly. The various deposition methods and resulting material properties makes the a-C coating attractive for various applications as it can enhance the material properties to fit the application.

This work demonstrated different deposition methods of transparent amorphous carbon coating. Using magnetron and single beam ion source, a-C coating with high transmittance of 90% at visible light wavelength. The coatings have wide range of mechanical properties depending on the method. The magnetron method with the lowest mechanical properties, ion source method with highest

mechanical properties while the dual method produced mechanical properties in between the other two methods. By combining the two devices, high deposition rate was achieved. The various deposition methods and resulting material properties makes the a-C coating attractive for various applications. The different methods were able to adjust mechanical properties of the coating. By tuning the deposition parameters such as RF power and selecting the processing method, it is possible to adjust the material properties and deposition rates.

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CHAPTER 5

SUMMARY AND FUTURE WORK

The work presented in this dissertation was aimed at improving the DLC coatings with different deposition methods in order to achieve necessary properties for high performance suitable for various applications. In the ‘duplex coating’ research, two different deposition methods were combined to produce a hybrid coating that was able to perform in harsh conditions of high loads and corrosive environment. In the ‘magnetron sputtering and ion source enhanced DLC coatings’ research, a new PECVD method was created with a single beam ion source and sputtering magnetron to create highly transparent and durable coatings for plastic substrates. This dissertation work has investigated the relationship between the material process, structure and performance and brought the gaps closer together.

5.1 Single Beam Ion Source

This research demonstrated that the single beam ion source was able to create carbon coatings with promising properties of combined high Young’s modulus and optical transmittance. The material properties were tunable by adjusting the deposition parameters. Continued research is required to study the full effects of the parameters on the material properties. By doing so, the extreme properties of DLC material and the capability of the deposition method can be fully deployed; DLC coatings tailored to a specific application can be manufactured.

The material structure could be investigated further. Using Raman spectroscopy and nuclear magnetic resonance (NMR) spectroscopy, the structure of the DLC could be investigated. Raman spectroscopy will be able to identify the sp^2 and sp^3 bonds. The peak arising at 1180 cm^{-1} corresponds to the vibration of carbon atoms bonded in sp^3 hybrid bonds. The peak intensity increases as the content of sp^3 bonds increased.

The peak at 1600 cm^{-1} corresponds to sp^2 hybrid bond vibrations. By fitting the two peaks with Gaussian peaks and calculating the intensity, it was possible to calculate the ratio of sp^2 and sp^3 hybrid bonds. By combining the data with NMR, the full picture of the DLC structure

could be analyzed. The analyses of the structure would also allow the understanding of the carbon bond distributions by investigating the formation of the sp^2 and sp^3 as clusters or randomly ordered chains. The relationship between the distribution of the bond structures and the material properties could be investigated. The material could also exhibit some crystallinity in the amorphous structure, which could be characterized by x-ray diffraction (XRD). The gap of knowledge between the material processing and structure could be brought closer, allowing better understanding of the effect the processing parameters have on the material properties.

Some of the parameters that need further study include power and reactive gas. The power parameter could be changed in order to achieve the optimal value of mechanical properties. The relationship between the ion energy and mechanical properties resembles a bell-shaped curve. Too much power could cause graphitization from the heat and surface etching, while too low power results in the formation of graphite structures in the material, which reduces the mechanical properties. The power parameter could be changed in lower increments to study the relationship between the applied power source and Young's modulus. The ion energy is proportional to applied power, so the relationship between the ion energy and applied power can be determined.

There have been studies to investigate the uniformity of the properties of the DLC coatings. It was discovered that the mechanical properties such as Young's modulus and hardness were higher, closer to the substrate than the surface. It showed that as the thickness of the coating increases, the material on the surface were weaker and exhibited more characteristics of graphite. It was theorized that the compressive stress is required for the formation of sp^3 bonds. The coatings on the surfaces do not have enough compressive stress to form sp^3 and form more of sp^2 hybrid bonds, making the coating weaker. It would be interesting to investigate the material structure and the change in power throughout the deposition process. If the power slowly increased at an interval during the process, it would be possible to produce DLC coating that is not weaker on the surface. By increasing the power, it could give the compressive stress the carbon atoms require to form the sp^3 bonds. With increasing thickness, the power should be increased to compensate for the decreasing compressive stress. The process could produce DLC coating that is not weaker on the surface and

exhibits structure that has more uniform distribution of sp^2 and sp^3 contents.

The usage of new gas source should be studied. Only one type of gas was used for this research, but the impact of other gases such as pure methane and acetylene on the material properties could be investigated. The DLC coatings should be deposited using the same pressure and power parameters as the previous research. To start the investigation, the research should be replicated while only changing the gas. It would be interesting to investigate how the usage of pure methane would be different from argon and methane mixture gas. With pure methane, the deposition rates would increase as more gas species are generated. The contribution of argon ions could be studied as well by characterizing the mechanical properties. It is not clear if the argon ions had positive or negative impacts. It could be that the argon ions caused an etching effect or promoted densification of the carbon ions.

The impact of the argon ions can be further studied by conducting post deposition treatment. After the deposition of DLC coating using pure methane, the ion source could be used as a post treatment process using pure argon gas. The kinetic energy from the argon ions could be used to promote formation of sp^3 hybrid bonds by increasing the compressive stress of the coating as well as densification of the coating as well. The pressure and the power should not be too high, as it could cause the etching of the coating on the surface and delamination if the etching is intensified. A systematic study could be conducted with increasing power, pressure and deposition time. Young's modulus and density could be calculated as the parameters are changed. The systemic study could show which parameter has the highest impact on the ability of the process to density the coating. An optimal value of the parameters could be calculated, which would increase the potential of the process greatly. A simple process that uses the same device as the deposition as post treatment would give the process a great advantage as it saves on cost, time and equipment.

By using the acetylene, the DLC coating properties are expected to change as well. Acetylene molecule is composed of more carbon atoms, but has less hydrogen atoms than methane. The higher carbon content would increase the plasma species with more carbon and result in higher DLC deposition rates. The power could be changed accordingly to promote the formation of sp^3

bonds. The post deposition process with argon gas could be used as well if the previous study shows improvements on the properties. Without additional hydrogen, the transmittance of the coatings could decrease as well. It was believed that the incorporation of the hydrogen in DLC coating causes the transparency of the material. When the hydrogen content in the gas is decreased, the content of hydrogen in the coating would decrease as well, resulting in a DLC coating with lower transmittance but more durable.

5.2 Nitrogen Doping

The single beam ion source was able to produce a highly transparent, durable DLC coating. Pure nitrogen could be used with methane gas to create a nitrogen doping process. This would make the coating transparent and conductive, which would widen the potential applications of the material. Examples of the potential applications include solar cells and electronics. Nitrogen doping of DLC by PECVD has been conducted in the past. However, the process has not been conducted with a single beam ion source that overcomes the limitations of current ion source PECVD methods. The previous research discussed the limitations and the advantages the single beam ion source has.

Electrical properties such as conductivity and resistivity should be characterized at different processing parameters to study the doping process of DLC. The study should introduce nitrogen at 10% and 90% methane to begin with, as a small amount of nitrogen has shown to reduce the resistivity of the DLC coating by previous studies. The structure of the resulting DLC material should be studied accordingly using the characterization methods mentioned above. It would be interesting to analyze how the nitrogen is incorporated into the DLC. If the nitrogen atom replaces the hydrogen atom, it could decrease the transparency of the material. On the other hand, nitrogen could bond with carbon ions and form compounds or terminate dangling bonds and promote the formation of sp^2 bonds, which would make the coatings softer. It would be interesting to investigate the relationship between the structure and electrical properties. The goal of the study would be to find the optimal parameters that would produce conductive DLC that does not sacrifice the high transparency and durability of the coating.

5.3 Linear Ion Source

By using a large linear ion source, large substrates could be deposited at a faster rate. The thickness of the coating could be measured at different positions of the substrate to investigate the deposition rate and the thickness uniformity. The research could be replicated using the linear ion source instead of the single beam ion source. The material properties could be compared to verify if the larger size ion source impacts the structure of the coatings. If there is no difference in the material properties other than the deposition rate, the process could be implemented with a process conveyor belt to scale up the process.

5.4 Dual Deposition

In this dissertation, the implementation of dual deposition with reactive magnetron sputtering and single beam ion source can produce DLC coatings with a wide range of Young's modulus without decreasing the transparency. It was mentioned that by using different methods, the DLC coating layers with gradual increase in Young's modulus could be deposited to reduce the sharp interface between the coating and substrate. Eliminating the sharp interface would improve the mechanical strength of the coatings and the adhesion between the coating and substrate. An example process includes firstly reactive magnetron deposition at 40 W RF power, followed by dual deposition at 40 W RF power for both magnetron and ion source, and finally ion source deposition at 40 W RF power. The deposition time can be changed accordingly to make sure that the thickness of each layer is optimal. In order to analyze the durability of the coatings, a scratch tests should be conducted with the gradual layer coating samples and ion source deposited DLC at 40 W RF power. The transmittance of the gradual layer coatings should be analyzed as well.

5.5 Sensor Moisture Barrier

A collaborative project has started to study transparent DLC coating as a moisture barrier for sensors. The project aims to determine if the carbon coating is suitable for multi-array sensor (MEA) packaging. The application requires a thin, yet durable coating that is transparent. Because this dissertation work has proven the formation of carbon coatings, the future research could focus on tuning the process parameters to fabricate material with the desired mechanical and optical

properties. The most interested property of the coating is O_2 barrier. PET plastic sheets coated with DLC films could be used to test O_2 transmission to determine the barrier capability. The microstructure plays the key role in the transmission of O_2 through the DLC coating. Therefore, it is necessary to investigate the concentrations of sp^2 and sp^3 bonds in the coatings.

The collaboration with Dr. Wen Li is on going. The project is studying the application of transparent DLC as a moisture barrier for medical sensors. The project is testing to analyze if the carbon coating is suitable for MEA packaging. The application requires a thin, yet durable coating that is transparent. Because the dissertation has proven the concept of the process, the team is tuning the process parameters to fabricate material with desired properties. The most interested property of the coating is O_2 barrier. The PET plastic sheets coated in DLC coatings could undergo O_2 a transmittance test to analyze the barrier capability. The structure of the material could impact the transportation of O_2 through the DLC coating. Also, the different distribution of sp^2 and sp^3 bonds could impact the transportation of O_2 molecules, as the dangling bonds could react with the oxygen molecules and form compounds. In the dissertation, the different deposition methods have produced material with different structures. By using the same deposition parameters, the coatings could be deposited on PET or parylene sheets. The material structure and O_2 barrier properties could be characterized to establish a relationship between the material structure and moisture barrier properties.