Biocompatible Nanomaterial TiN, ZrN and TiAlN Thinfilms Coating on Surgical Tools by Cathodic Arc Deposition

Saba Zafar [1*]

Abstract

Background: Thin film coating is a widely employed process across industries such as electronics, optics, solar energy, and aerospace to enhance surface properties or improve performance. The process can be carried out using various methods, including physical vapor deposition (PVD) and chemical vapor deposition (CVD). Cathodic arc deposition, a PVD technique, is notable for its ability to produce thin films of materials like titanium nitride (TiN), zirconium nitride (ZrN), and titanium aluminum nitride (TiAlN), which are valued for their hardness, wear resistance, and biocompatibility, making them suitable for coating surgical tools. Methods: This study utilized cathodic arc deposition to produce TiN, ZrN, and TiAlN thin films on 316 stainless steel substrates. In the cathodic arc deposition process, a high-voltage electrical discharge is generated between a cathode target material and an anode within a vacuum chamber. This discharge vaporizes the target material, creating a plasma that condenses onto the substrate, forming a thin film. The hardness of the materials and Raman spectroscopy were used to characterize and compare the three thin films. Raman spectroscopy was employed to gather information on molecular bonding, crystal structure, and chemical composition. Results: The characterization revealed that both ZrN and TiN thin films demonstrated superior hardness, which contributes to good adhesion, Wear resistance, and biocompatible properties essential for coating surgical tools. The Raman spectroscopy results provided detailed insights into the molecular bonding, crystal structures, and chemical compositions of the films. The ZrN and TiN films were found to be particularly suitable for depositing colored thin films on surgical tools due to their high hardness. Conclusion: The study confirms that TiN and ZrN thin films produced via cathodic arc deposition are highly suitable for coating surgical tools, owing to their excellent hardness, adhesion, wear resistance, and biocompatibility. These properties make them ideal for applications where durability and biocompatibility are critical. Further research is required to explore various decorative color coatings on surgical tools that maintain biocompatibility, enhancing both the functional and aesthetic aspects of these tools

Keywords: Thin film technology, Surface modifications, Titanium nitride (TiN), Surgical tools, Cathodic arc deposition, Coating.

Significance | This is a study of advancements in Thin Film Deposition for Enhanced Performance of Surgical Tools. This study improves surgical tools by using thin film coatings, enhancing durability, corrosion resistance, and performance, while reducing costs.

*Correspondence.

Saba Zafar, National Center for Physics, Shahdra Valley Road, Islamabad 44000, Pakistan
Email: szbutt11@gmail.com

Introduction

Thin film technology is a large branch of the generic technology that has to do with surface modifications and coatings. In the surface modification process the properties of the surface of the substrate material is changed, as exemplified by the hardening of steel surface by introducing carbon or nitrogen to the surface or as in doping of semiconductors to change its electrical conductivity. In the process

that involves the application of a coating, the substrate material and the coating may be quite different, as exemplified by the deposition of aluminum or chromium on polymer surfaces or deposition of a hard coating of titanium nitride on tool bits. The features of the process are important to form the desired modification of the surface are, to consider the role of background pressure, concentration of impurities in the vapor phase, kinetic energy of the incident particles, deposition rate, nature of substrate material, temperature of the substrate and its surface cleanliness, orientation and microstructure.

All these have an effect on the type of microstructure of the film that is formed. Thin film exhibit following types of properties, a low-resistivity film is required in superconducting films; a high breakdown voltage is the essential feature for a dielectric film and so on. Each of these properties is dependent on the structure of thin film, which in turn depends on the process used to attain the film. It is convenient to study the methods of thin film deposition in four stages. In the first stage, we focus attention on the principles and methods underlying the formation of the vapor phase from the condensed phase and the properties of the vapor. Evaporation, electron beam evaporation, sputtering, ion deposition and so on describe some method of vapor creation. The transport of atoms or molecules from the source to the substrate constitutes the second stage. The third stage involves the deposition of atoms on the substrate.

The final stage involves those processes that allow us to rearrange the atoms on the film or reconfigure the geometry of the film to give the desired properties for the product. In order to produce commercial products, it is necessary to identify and develops the techniques that will allow the economical manufacture of large area films of these materials. The nature of the movement of atoms from source to substrate will determine the uniformity of the film that one can obtain. The actual properties of the film depend on the substrate chosen and its surface preparation. The technology of thin films covers a wide spectrum spanning the thicknesses from a few nanometers to one micron.

One of the simplest reasons is that we desire to produce properties in a material that are often conflicting in nature if we use one homogeneous material. Semiconductor devices, for example, are fabricated on a thin layer deposited on a semiconductor substrate. The integrated electronic circuits depend on the confinement of electrical charges, which relies on the interfaces between different materials with differing electronic properties. There are also many occasions when the properties demanded for an engineering application involve features that are different for the surface that are for the bulk. Deposition metal films and pattering them on the surface are relatively easy to secure electrical connection between semiconductor devices. Creating a composite material, such as a bulk material with a coating of a thin film, is a design flexibility that can achieve the desired properties.

The surface and near surface properties are important in altering the functionality of the material and extend service life (corrosion, wear, erosion etc). Titanium nitride coatings on tool bits offer hardness reduce friction and provide a chemical barrier of the tool to alloying with the work piece. The deposition of films, such as chromium for corrosion protection and titanium nitride for improving wear resistance are important in improving product life. Thin films are a good alternative to economic manufacture of products. Thin films by mechanical deformation of bulk material require excessive number of annealing stages to make their preparation prohibitively uneconomical. Even when the bulk material can perform a desired function, it may be necessary to use the material in a thin film form on some other suitable less expensive and widely available material. This option in design eliminates the need to use costly material in bulk form, thereby saving precious resources and conserve materials. Thin films offer a unique design opportunity and flexibility to create products in a very cost effective way. It is useful to discuss the formation of thin films as belonging to the category of physical or chemical deposition methods. We tentatively think of the deposit to have the same composition as the source in a physical method, whereas the chemical method alters the composition of the film from that of the sources.

Physical deposition methods are very general with respect to either the material to be deposited or the specific substrate, so that it is useful to become familiar with the principle in these methods. A number of requirements to be met by thin films deposited by any method are: choice of substrate, growth rate, uniformity of deposit, wide window of processing, adaptability to different conditions of operation, cost of ownership, compactness when many machines are required, low generation of particulates so that the number of successful runs between cleaning cycles is large, reproducibility, throughput, yield and reliability of the product and concerns about the materials used in the reactor interfering with the process.

The technology of thin film deposition receives its impetus for growth from the increased performance, reduced costs and control of properties different than that of the substrate. These features have permitted the addition of and development of entirely new products, provided additional features in design and manufacturing, permits the achievement of improved functionality in the products, conserves resources and materials and reduced the wastes encountered in traditional manufacturing. The properties of material as affected by the quantum confinement of charge carries have opened up the entire field of nano-structures. The electronic, magnetic and optical properties of thin films are the key to the convergence of computing, communications and consumer electronics. Coating produced on short time implants for medical

use, such as surgical tools, coated for instance with TiN thin films, is an interesting practical application of thin film (Harsha et al ,2005). {[The tools which are used for surgical purposes are called surgical tools e.g. tools used for heart operation and kidney operation as well as artificial teeth purposes, such as scalpels, scissors, elevators, curettes, vice grips, surgical nails and screws etc. When cutting tools are first used, they develop a wear land during the break-in period. The wear of cutting edge then proceeds at a much slower space, this is called the low wear period. The useful life of the tool continues until rapid edge breakdown begins to occur. At this time, the tool should be sharpened. When a tool is coated, the low wear period is extended for beyond that of uncoated tools. There are number of reports detailing dramatic improvements in tools life and productivity due to the use of TiN-coated drills, end mills, milling cutters and other high speed steel tools. TiN coated tools are now used on all metal removal operations to extend tool life, increase speed and reduce machine downtime. Three areas should be considered by those who would like to understand the advantages of coated tools the tool quality, the consistency of the quality and the tool performance. Surgical tools and instruments must have certain characteristics in order to qualify for medical use. These characteristics include hardness, nick free cutting edges and corrosion free surfaces. Such tools are usually manufactured using 300 series stainless steel. The 300 series stainless steels are low carbon stainless steels such as 316, 304 etc. such steels are sterilized easily and have high mechanical strength. Therefore the most important kinds of stainless steel for producing surgical tools are low carbon stainless steels. However such steels are relative susceptible to corrosion and extreme care must be taken with their storage.

The cost of surgical tools and instruments made of low carbon stainless steel is very high. These costly surgical tools and instruments have a short life time due to their rapid corrosion. So we use coating on surgical tools and instruments for corrosion resistance. All such instruments and tools are sterilized after each use. Generally, tools and instruments used for surgical purposes are soaked in a concentrated solution of caustic and then steam/gas sterilized in an autoclave after each use. Usually steam sterilization was performed in an autoclave by keeping the sterilization pressure at three steps (1, 2 and 3 bar). The temperature is nearly 130 C° and sterilization time was adjusted prescribed values by technical standards. In addition, a standardized spray test with sodium chloride solution was carried out. Both these processes soaking and autoclaving processes quickly enhance the oxidation or corrosion of tool surfaces. The costly surgical tools and instruments that are presently used in surgery and medical applications are often become useless due to rapid corrosion after just 5 to 10 uses.

Due to the presence of nickel in stain less steel, nickel allergy problems occurred, which restricts surgical operations in some

cases, a spherical emphasis was the study of nickel diffusion into the coated layers.304 stainless steel contain about 9 wt% of nickel. One of the important asked questions arising from the surgical instrument industry is whether nickel can penetrate into the coated layers. Due to this reason we consider nickel diffusion after steam sterilization. However, as expected, no abnormal nickel amount was investigated in any of the investigated species; i.e. no nickel element of the substrate material including nickel was observed.The coated surgical tools and instruments have many advantages over uncoated tools and instruments. Because of the hard surface produced, the medical tools and instruments can be used many times without resharpening any sharp or cutting edges. The coating also provides better cycles of utilization, caustic soak and steam sterilization. Moreover decorative coated tools are seemed attractive.

Another reason for coating surgical tools is that low-reflective top layers are particularly important for tools used in surgery. The reflection and scattering of bright light from the surfaces of the tools can create disturbances for the surgeon during an operation. To decrease this type of disturbance, a thin film of black color is used as a possible precaution (Van Raay et al., 1995). To produce black PVD coatings, one can resort to the well-known field of decorative coatings. The main industrial and best-investigated solution for dark colors is sputtered tertiary TiAlN and TiCN layers (Münz, 1986; Hsieh et al., 1998). However, these single layers do not seem to be dense enough to protect the substrate against corrosion. The substrate can be particularly affected by the multiple sterilizations of the instruments (Louw et al., 1991). In order to coat instruments and tools suited for surgical purposes, the coating should have excellent corrosion resistance, wear resistance, and good adhesion. This can be achieved by selecting a suitable coating, such as decorative coatings and coating techniques.

A coating whose function is to decorate so that the properties of interest are primarily color, color distribution, and reflectivity is called decorative coating. Decorative coating was first introduced on small parts such as watches, writing instruments, buttons, and rings. Since the development of new coating sources and techniques that allow expanding the plasma of the cathode discharge into large spaces, coating of large parts or part arrangements such as chains and frames with decorative hard layers is possible (Hofmann et al., 1991). The compound and alloy materials of decorative coatings have extraordinary micro-hardness and a suitable ability to resist environmental wear. In addition, the energetic deposition processes involved encourage high packing density, which leads to increased hardness (Mitterer et al., 1996). The quantum mechanical selection rules for electron transitions can force electrons to return to lower levels via different paths than their excitation, and the color of emitted light may not correspond to the absorbed light,

contributing to color appearance (Martin, 2009). Optical coatings have been deposited simply by evaporating the compound using an electron beam evaporation source. The coatings thus produced are invariably non-stoichiometric. To improve the stoichiometry and thus the refractive index of the coating, the reactive evaporation method was subsequently used. Next, plasma-enhanced evaporation techniques were developed to obtain better control of stoichiometry. One such technique, called the reactive evaporation process, has been used to deposit a number of optical films (Hofmann et al., 1996). Many colors can be produced by sputtering alloys of metals, such as alloys of Cr, Ni, Au, and Cu, or by reactive plasma deposition of compounds such as TiN, ZrN, CrxN, and ZrCxNy. The TiN system has evolved into Ti-Al-N, Ti-Zr-N, and Ti-Al-Zr-N systems, each with particular benefits in wear and corrosion resistance. Decorative coatings are produced by transition metals, noble metals, and alloys, as well as compounds (Reiners et al., 1994). When binary materials such as TiN, TiC, and ZrN are reacted with O, N, or C, or alloyed with another metal, the range of color possibilities is expanded, with reactive sputtering and cathodic arc deposition techniques (Randhawa, 1988). In the TiN and ZrN systems, color is varied with nitrogen percentage. Colors can be stabilized by adding carbon, which probably modifies the microstructure of the layer (Schlegel et al., 1977). A gold-like appearance of these materials results from the high reflectance of the materials at the red end of the visible spectrum with low reflectance near the ultraviolet region (Logothetidis et al., 1995). The stoichiometric variation of thin film composition causes variance in free electron concentration, which mainly affects the reflectivity and color of nitrides (Kuznetsov et al., 1992; Bendavid et al., 1996). According to the ionic model of transition metal nitrides, free electrons in the d orbital of transition metal atoms are transferred to nitrogen atoms to form transition metal nitrides. Increasing nitrogen atoms results in the reduction of free electrons in these nitrides. Therefore, fewer electrons interact with incident light, reducing the reflected light in the nitride thin films (Wert & Thomson, 1964; Zallen, 1966). Light is absorbed through many absorption mechanisms before it is examined as color after leaving the surface of a material. The absorption takes place due to the response of both optical phonons and outermost electrons. The absorption processes are categorized into four types of mechanisms: Reststrahlen absorption; interband transition; absorption due to impurities; and free-carrier absorption (Nassau, 1980). The transition of electrons occurs between two different bands (Loeffler & Burns, 1976). Color appears from the remaining visible light other than the absorbed threshold energy. Color produced in this process depends on the energy value of the band gap. With band gaps larger than 3.5 eV (ultraviolet), for example, diamond with 5.6 eV Eg, the materials become transparent because visible light is not absorbed. Materials with band gaps smaller than 1.7 eV (infrared),

such as silicon with 1.11 eV Eg, are non-transparent and blackish due to the absorption of the whole visible light. With band gaps lying within the range of the visible region (1.7 eV < Eg < 3.5 eV), the particular threshold energies within the visible region are absorbed, producing characteristic colors in materials. In imperfect crystals, there are some extra energy levels located in a small region around defects. Ground state electrons then require photons of lower energy than in perfect crystals to go to the higher energy states. Therefore, absorption of photons in the visible range may take place, resulting in the production of color (Bube, 1992). For example, diamond (colorless) turns yellowish with nitrogen doping (Niyomsoan et al., 2002). The main absorption mechanism of the present study is intraband transition or free-carrier absorption. As oxygen replaces nitrogen in nitrides, oxygen behaves as if it were nitrogen, consuming d electrons from the transition metal (Karlsson et al., 2000). Titanium and zirconium belong to the same periodic element group, but Zr-based coatings are more chemically resistant than Ti-based ones with regard to some relevant environmental loadings (Witke et al., 2000). To estimate the biotoleration of a PVD hard coating, a simple method is the observation and evaluation of the growth of certain animal cells. Regarding the biocompatibility of ZrCN thin film ceramics, it was demonstrated that all of the investigated coatings have fulfilled the requirements for short-term applications to the human body (Hollstein et al., 2001).

A variety of process technologies are available for the deposition of thin films. These technologies differ significantly in their physical and chemical principles of operation and in the commercially available types of equipment. Chemical vapor deposition (CVD) is a material deposition process where a mixture of gases reacts chemically on a substrate surface to form a solid product (Mattox, 1999). Incandescent lamps are one example of CVD (Sherwood & Blocher, 1965). Chemical vapor deposition is deposited at a slow rate, usually a few hundred microns per hour; this is another disadvantage of the chemical vapor deposition method (Ohring, 2001). Physical vapor deposition (PVD) is basically a vaporization coating technique in which film is deposited atom by atom. Physical vapor deposition processes are carried out under vacuum conditions. The process consists of four steps: evaporation, transportation, reaction, and deposition. In PVD, the substrate can range in shape from flat to complex geometries. Physical vapor deposition processes can be used to deposit films of elements, mixtures, alloys, and compounds using reactive deposition. Physical vapor deposition is classified into sputtering (Mattox, 1999), pulsed laser deposition (Ohring, 2001), electron beam evaporation (Wolfe & Singh, 2000), reactive sputter deposition (Sproul, 1996), and cathodic arc deposition (Tracton, 2005; Boercker et al., 1992).

Materials and Methods

The experiment was done by using cathodic arc deposition technique, at "Quench Age" Sialkot Pakistan. The cathodic arc system is shown in fig. 1.1

The cathodic arc deposition system consists of following components: the deposition chamber, pumping system and control system.

Cathode target was fixed upon a water cooled support placed inside the chamber and an anode disc was placed around the cathode. A trigger electrode wire was attached to cathode. A moveable holder was placed in front of the cathode. The substrate was placed on the rotating holder which was rotated continuously by its axis to provide a uniform coating. The average distance between the substrate holder and the target was 18cm. Pumping system consists of three pumps vacuum pump, booster and turbo pump. Vacuum pump produces vacuum up to 10^{-2} Pa. To maintain this pressure booster was used. During the flow of nitrogen gas in chamber, turbo pump was used to maintain pressure at specific limit.

As the setup is manual so from control system we adjusted the value of arc current, arc voltage and substrate biasing. It also shows the deposition chamber base pressure and chamber temperature. It was also used to control the nitrogen flow rate and nitrogen pressure. For this experiment stainless steel 316 was used as a substrate. To prepare decorative thin films different source materials such as titanium, zirconium and titanium aluminum were used. Before coating proper cleaning of substrate is necessary. Almost whole substrate surfaces should be considered as contaminated. It is necessary to be sure that whole surface of substrate is clean as well as dry. Any moisture can cause premature failure by bubbling, reason adhesion loss and therefore reduce the durability and performance degree. Quench Age offered two cleaning methods.

➢ Ultrasonic cleaning by deionized water
➢ Gas cleaning

Ultrasonic cleaning provided the cleaning method required for a very high degree of precision cleaning. Ultrasonic liquid cavitation is the formation and implosion of very small vacuum bubbles that remove contaminate from the substrate surface. Ultrasonic sound waves fill the bath with alternating low and high pressure zones at frequencies of 20-180 KHz. During the low pressure zone, liquid molecules are pulled apart forming microscopic vacuum bubbles and then on high side of the ultrasonic wave, the bubble implodes. The implosion of bubble releases energy which releases the contaminants from substrate.

After ultrasonic cleaning the substrate is dried, for this purpose we used a heat gun to remove moisture. After drying the substrate we created the vacuum using the vacuum pump. Vacuum pump creates a pressure of 10^{-2} Pa. After achieving this value of pressure

in chamber the substrate was put on into the chamber on a rotating substrate holder and argon gas was filled into the chamber. The next step was gas cleaning for which an argon based cleaning process is suitable because argon is an inert gas so it removes all kinds of impurities from the surface of substrate without causing a chemical reaction on the surface of the substrate. During the gas cleaning pressure reduces to 10^{0} Pa. Finally for deposition we readjusted the base pressure of chamber at about 1.6×10^{-2} Pa. Nitrogen gas was filled into the chamber and was used as reactive gas. A low voltage high current dc arc power supply was used for cathode target vaporization. The substrate was rotated in front of target material and deposition was started.

Colored thin films were prepared using different materials. First of all a golden colored thin film was prepared. In order to prepare golden color thin film titanium was used as a target material and nitrogen gas as a reactive gas. Stainless steel 316 was used as a substrate. After putting the target material and substrate into the chamber, the base pressure was fixed at 1.6×10^{-2} pa. Low voltage, high current DC arc power supply was adjusted such as the arc voltage was 20V and arc current was 75A. The temperature during deposition was recorded about 120^{0}C and deposition timing was 4 minutes. A summary of the deposition parameters can be seen in Table 1.1

As the vaporized titanium (cathode target) passed through the arc, it ionized and plasma was produced which consists of electrons, ions as well as neutral particles. The plasma was directed towards the substrate's surface and in the presence of nitrogen form a TiN coating of golden color.

Secondly a light gold colored thin film was prepared. For this purpose zirconium was used as a target material and nitrogen gas was filled into the chamber. Substrate was same as in previous case. After putting the source material and substrate into the chamber, the base pressure was fixed at 1.6×10^{-2} Pa. The substrate was biased such as the bias voltage was 150V. An arc was used to vaporize the source material. The temperature during deposition was recorded about 105^{0}C. A summary of the deposition parameters is given in the table 1.2

As the vaporized zirconium (cathode target) passed through the arc, it ionized forming plasma. The plasma was directed towards the substrate's surface and in the presence of nitrogen form a ZrN coating of light gold like color. Thirdly a brown colored thin film was prepared. In order to prepare brown color thin film titanium aluminum was used as a target material and nitrogen gas as a reactive gas and stainless steel 316 was used as a substrate.

After putting the target material and substrate into the chamber, the base pressure was fixed at 5.8×10^{-2} Pa. Low voltage, high current DC arc power supply was adjusted such as the arc voltage was 20V and arc current was 75A. The temperature during deposition was
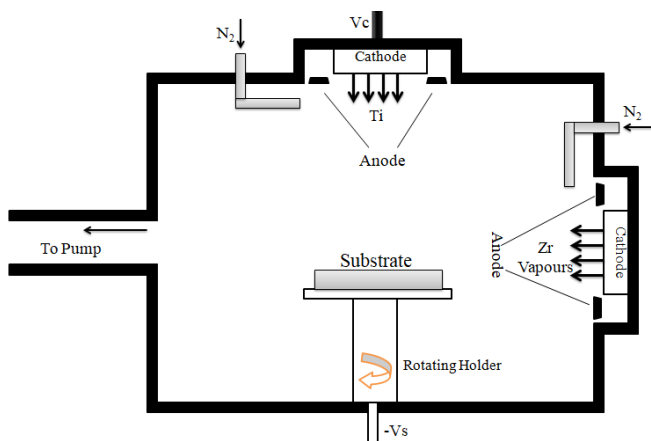
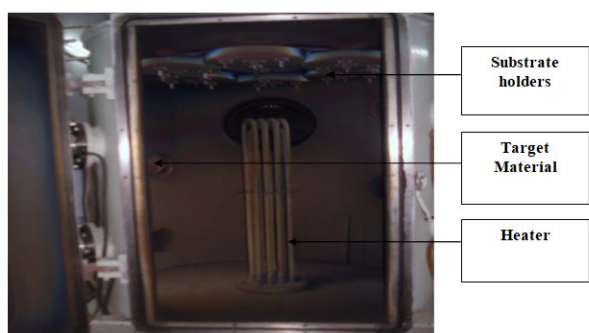**Figure 1.1**. Schematic illustration of the deposition setup.
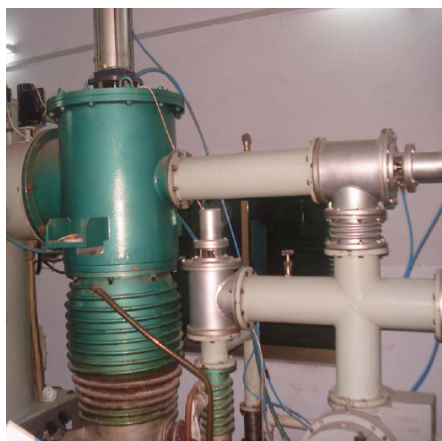

Figure 1.2 Deposition chamber

Figure 1.3 Pumping System

Table 2.3:   Hardness values of TiAlN at different loads.

Load (grams)	Hardness value (HV)	Hardness value (GPa)
10	1740.4	17.07
25	1580.85	15.5
50	1380	13.53
100	1220.57	11.97
200	1195.12	11.72
300	1170.77	11.47
500	1160.4	11.37

Table 3.1: Summary of Deposition Parameters for TiN

Substrate material	316 stainless steel
Cathode material	Titanium
Reactive atmosphere	Nitrogen gas
Base pressure	1.7×10^{-2} Pa
Substrate biasing	150 V
Arc current	75A
Arc voltage	20V
Chamber temperature	120 ^{0}C
Nitrogen flow rate	48 Sccm
Nitrogen pressure	0.35 bar
Coating color	golden
Deposition time	4 min.

Table 1.2: Summary of Deposition Parameters for ZrN

Substrate material	316 stainless steel
Cathode material	Zirconium
Reactive atmosphere	Nitrogen gas
Base pressure	1.7×10^{-2} Pa
Substrate biasing	150 V
Arc current	75A
Arc voltage	20V
Chamber temperature	105^{0}C
Nitrogen flow rate	48 Sccm
Nitrogen pressure	0.35 bar
Coating color	Light gold
Deposition time	4 min.

Table 3.2 Deposition parameters is listed

Substrate material	316 stainless steel
Cathode material	Titanium aluminum
Reactive atmosphere	Nitrogen gas
Base pressure	5.8×10^{-2} Pa
Substrate biasing	150 V
Arc current	75A
Arc voltage	20V
Chamber temperature	111 ^{0}C
Nitrogen flow rate	78 Sccm
Nitrogen pressure	0.35 bar
Coating color	brown
Deposition time	4 min.

Table 2.2: Hardness values of ZrN at different loads.

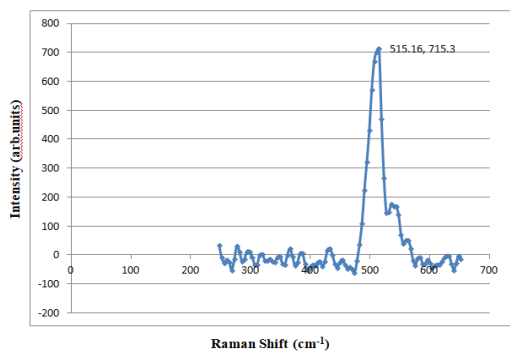| Load (grams)	Hardness value (HV)	Hardness value (GPa)
10	2420.88	23.74
25	1950.66	19.13
50	1660.25	16.27
100	1350.57	13.25
200	1210.57	11.87
300	1220.16	11.97
500	1190.37	11.67

Figure 2.1 Raman spectra peak of Titanium Nitride (TiN) thin film.
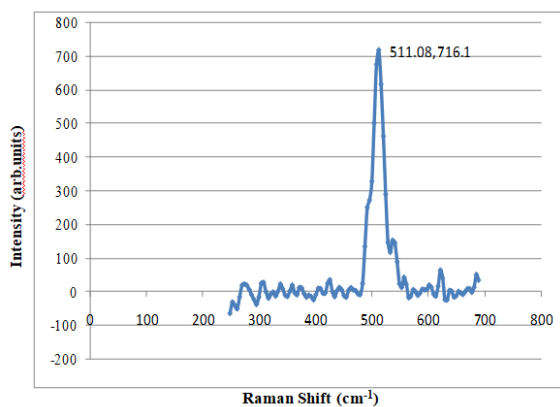

Figure 2.2 Raman spectra peak of Zirconium Nitride (ZrN) thin film.
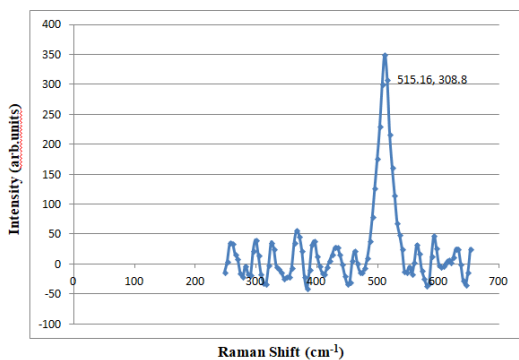

Figure 2.3 Raman spectra peak of Titanium Aluminum Nitride (TiAlN) thin film.

Table 2.2 Giga Pascal listed

Load (grams)	Hardness value (HV)	Hardness value (GPa)
10	2240.2	21.97
25	2020.38	19.81
50	1660.66	16.29
100	1410	13.83
200	1261	12.36
300	1220.75	11.97
500	1190	11.68

- HV = Vickers hardness
- GPa= Giga Pascal
- To convert HV to GPa multiply by 0.00980

recorded about 111⁰C and deposition timing was 4 minutes. A summary of the deposition parameters is listed in Table 1.3

As the vaporized titanium aluminum (cathode target) passed through the arc, it ionized forming plasma. The plasma was directed towards the substrate's surface and in the presence of nitrogen form a TiAlN coating of brown like color.

Results and discussion

The films are characterized by Raman spectroscopy and hardness is measured by Vickers micro hardness tester. Raman spectroscopy is a technique used to study the vibrational modes of molecules by measuring the scattering of monochromatic light. When a sample is exposed to a laser light source, the molecules within the sample scatter the light in different directions based on their vibrational energy levels. This scattered light, known as Raman scattering, contains valuable information about the molecular structure and composition of the sample.

Raman spectroscopy is widely used in various fields such as chemistry, materials science, biology, and pharmaceuticals. It can provide information on molecular bonding, crystal structure, and chemical composition of materials. This technique is non-destructive and can be used to analyze samples in various states, such as solids, liquids, and gases.

Decorative colored thin films are prepared using TiN, TiAlN, and ZrN materials. The colors of TiN, TiAlN, and ZrN films are golden, brown, and light gold, respectively. The color of TiN and ZrN films varies with nitrogen content (Niyomsoan et al., 2002). All films are analyzed by Raman spectroscopy. Raman analysis has been performed using a Renishaw Micro Raman Spectrometer by a laser beam of 814 nm with a spectral resolution of 4-5 cm⁻¹. The Raman pattern of the titanium nitride film is shown in Figure 2.1. The Raman spectrum of the Zirconium Nitride (ZrN) film deposited on stainless steel 316 is shown in Figure 2.2. The Raman pattern of the TiAlN sample is shown in Figure 2.3. As shown in the above figures, the peak of the titanium nitride film is at 515.16 cm⁻¹, the peak of the zirconium nitride film is at 511.08 cm⁻¹, and the Raman spectra peak of the titanium aluminum nitride thin film is shown at 515.16 cm⁻¹. Peak positions reported by Barshilia and Rajam (2004) and Constable et al. (1999) using magnetron sputtering for TiN, ZrN, and TiAlN are 562 cm⁻¹, 500 cm⁻¹, and 623 cm⁻¹, respectively. While in our case, the peak position is not the same. The reason is that the deposition technique and the experimental parameters were not the same.

As these colored thin films are fabricated on surgical tools, beside the color, we also have to examine the hardness of these films because hardness is the main characteristic of any thin film deposited on surgical tools (Martin, 2009). The hardness of the films is measured by a Vickers microhardness tester.Wilon Wolpert 401 MVA Vicker hardness tester is used to measure the surface hardness of deposited films for different loads. Hardness analysis of samples is carried out at loads 10, 25, 50, 100, 200, 300, 500 grams. These loads are applied on samples and resistance offered by samples to deformation is presented in vicker unit HV. The value of hardness of titanium nitride film in vicker hardness and Giga Pascal is given in table 2.1

The value of hardness of zirconium nitride sample in Vicker hardness and in Giga Pascal is listed in table 2.2

The value of hardness of titanium aluminum nitride determined from Vickers microhardness test is given in table 2.3

Our maximum micro hardness values for titanium nitride, zirconium nitride and titanium aluminum nitride films are 21.97GPa, 23.74GPa and17.07GPa respectively at 10 gram load. By comparing the value of hardness of above samples it is clear that zirconium nitride has highest value of hardness, second high value is of titanium nitride and titanium aluminum nitride has lower value of hardness.

TiN, ZrN and TiAlN films were deposited on SS 316 using cathodic arc technique. These films were confirmed by Raman spectroscopy. Zirconium nitride and titanium nitride films have high hardness as compared to titanium aluminum nitride.

Conclusion

Zirconium nitride and titanium nitride are more suitable for depositing colored thin films on surgical tools due to the high hardness. Due to high hardness TiN and ZrN films give good adhesion, wear resistance and biocompatible properties for coating surgical tools. However various research works have to be conducted to discuss the different decorative color coatings on surgical tools which show biocompatibility as well.

Color of titanium nitride and zirconium nitride thin films varies with nitrogen pressure and deposition parameters. ZrCN film gives black color which has good absorption of light well for aesthetic value for the surgeon. A wide range of colors can be obtained from titanium oxide by varying the amount of oxygen.

Author contributions

S.Z. formulated the study objectives, constructed the hypotheses, conducted the literature review, collected and analyzed the data, and revised the manuscript. The author approved the final version of the manuscript.

Competing financial interests

The authors have no conflict of interest.

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