CHARACTERIZATION OF ZrN THIN FILMS FOR LOW TEMPERATURE SENSORS IN DEEP SPACE APPLICATIONS

PROJECT REPORT

Submitted in partial fulfillment of the requirements for the award of the Degree of Master of Technology in Department of Electronics and Communication Engineering with specialization in Communication Systems by the APJ Abdul Kalam Technological University

by

PARVATHY S NAIR

TKM20ECCS10

DEPARTMENT OF ELECTRONICS AND COMMUNICATION ENGINEERING

TKM COLLEGE OF ENGINEERING

KOLLAM 691 005

2022

CHARACTERIZATION OF ZrN THIN FILMS FOR LOW TEMPERATURE SENSORS IN DEEP SPACE APPLICATION

PROJECT REPORT

Submitted in partial fulfillment of the requirements for the award of the Degree of Master of Technology in Electronics and Communication Engineering with specialization in Communication Systems Engineering by the APJ Abdul Kalam Technological University

by

PARVATHY S NAIR

(TKM20ECCS10)

DEPARTMENT OF ELECTRONICS AND COMMUNICATION ENGINEERING

TKM COLLEGE OF ENGINEERING

KOLLAM 691 005

2022

DEPARTMENT OF ELECTRONICS AND COMMUNICATION ENGINEERING

TKM COLLEGE OF ENGINEERING

KOLLAM 691 005

CERTIFICATE

*Certified that this project titled **"Characterization Of ZrN Thin Films For Low Temperature Sensors In Deep Space Applications"** is a bonafide record of the work done by **PARVATHY S NAIR** (Reg. No. TKM20ECCS10) under my supervision, in partial fulfillment of the requirements for the award of the Degree of Master of Technology in Electronics and Communication Engineering with specialization in Communication Systems by the APJ Abdul Kalam Technological University.*

Guide
Prof. ANU ASSIS
Associate Professor
Dept. of ECE, TKMCE

Coordinator
Dr. NISHANTH.N
Associate Professor
Dept. of ECE, TKMCE

HoD
Prof. ABID HUSSAIN
Head, Dept. of ECE
TKMCE

Acknowledgement

It is with immense joy and satisfaction that this work was completed. The project and its adjoined report would have never been possible if I had not received the abundant help from my professors. And hence I would like to take this opportunity to thank those helping hands that crafted the success out of my work. First I would like to extend my gratitude to, Prof. Abid Hussain Muhammed, HOD, Department of Electronics and Communication , for his support and encouragement.

Next, I would like to thank, the PG Coordinator, Dr. Nishanth N,Associate Professor, Department of Electronics and Communication Engineering, for the support and encouragement during the course of this project for his patience, and wholehearted suggestions in the entire course of this report preparation.

I express my heartfelt gratitude to my project guide, Prof Anu Assis, who stood by me and guided me through the process. I also take this opportunity to thank the entire faculty of the Department of ECE, TKMCE and my dearest friends for their wholehearted support in the completion of my work.

The completion of this work would not have been possible without the immense help I received from Dr S Kasthurirenga, Retired professor, IISc Bangalore, as well as the faculty and staff of the Center for Cryogenic Technology, IISc Bangalore.

I also express my heartfelt thanks to all my teachers, friends and my parents for providing the much-needed support during the course of preparation and execution of the project.

Parvathy S Nair

TKM20ECCS10

ABSTRACT

Zirconium-based coatings exhibit a range of useful properties such as high hardness, high temperature stability, biocompatibility, and good resistance to wear, erosion, corrosion and oxidation, making them suitable candidates for use in tribological, biomedical, corrosion-resistant, nuclear fuel, electrical and decorative applications. This work aims at fabricating and characterizing a ZrN thin film sensor of thickness between 200 to 300nm exhibiting a low negetive temperature coefficient of resistance using the RF Magnetron Sputtering mechanism. The Partial pressures of the reactive gas was varied in steps such that a low value of negetive temperature coefficient is obtained. it was found that for a ZrN thin film formed under the duration of 30 minutes, the lowest NTCR is obtained at the nitrogen partial pressure of 3×10^{-3}mbar and on comparison, exhibits desireable characteristics of sensors suited for deep space applications

Contents

Acknowledgement **ii**

Abstract **iii**

List of Figures **iv**

List of Tables **v**

1 Introduction **1**

Nomenclature **1**

2 Literature Review **3**

3 Fabrication and Characterization ZrN Thin Film **12**

3.1 Thin Film Deposition and Characterization 12

4 Results **16**

4.1 Obtaining the Sample Thickness 16

4.2 Obtaining the Lowest Negetive Temperature Coefficient 17

4.2.1 N_2 Partial Pressure at 2×10^{-3}mbar. 17

4.2.2 N_2 Partial Pressure at 2.5×10^{-3}mbar. 18

4.2.3 N_2 Partial Pressure at 3×10^{-3}mbar. 19

4.3 Comparison of ZrN Thin Film Generated with Si and Pt RTD 20

5 Conclusion **22**

References 23

List of Figures

3.1 Schematic Illustration of Magnetron Sputtering Method 13

3.2 RF Magnetron sputtering equipment 14

3.3 Mass Flow Controller 14

3.4 Two-stage GM Cryo-cooler 15

4.1 Variation in Thickness of ZrN Thin Film with Temperature 16

4.2 Variation in resistance of ZrN thin film with temperature at N2 partial pressure of 2×10^{-3}mbar 18

4.3 Variation in resistance of ZrN thin film with temperature at N2 partial pressure of 2.5×10^{-3}mbar 19

4.4 Variation in resistance of ZrN thin film with temperature at N2 partial pressure of 3×10^{-3}mbar 20

4.5 Variation in resistance with temperature of Platinum RTD, Silicon RTD, and ZrN Thin Film. 21

List of Tables

4.1 Comparison of NTCR at different partial pressures of N_2 20

4.2 Variation in resistance with temperature ZrN Thin Film Silicon and Platinum Resistance Temperature Detectors. 21

Chapter 1

Introduction

Zirconium is found in baddeleyite and ores such as zircon, and was initially reported by Martin Heinrich Klaproth in 1789 and separated by Jons Jacob Berzelius in 1824. In nature, zirconium is found as one long radioisotope and four stable isotopes. [1] (^{96}Zr) Zirconium-based ores were widely used for a variety of applications, including ceramic opacification, foundry work, refractories, and so on. Today, zirconium is used in corrosion-resistant pipes, nuclear cladding, fuel cells, solid electrolytes in oxygen sensors, and other applications. The key features of zirconium, including its high temperature ionic conductivity, corrosion resistance, good wear resistance, increased fracture toughness, and high hardness and strength, are used in these applications. The thermal expansion and modulus of elasticity of zirconium are comparable to those of iron and steel, respectively. These characteristics have led to zirconium-based materials being used in protective coatings for mechanical, chemical, and biological applications, among others.
the 1960s to the 1970s, it was realised that sintered ZrN materials may be used in machine tools. [2] Carbon fibres were coated with ZrN by Zabolotskii et al. in 1977. [3] Caillet et al. [1] investigated zirconium nitride as a metal covering in 1977.The coating's oxidation kinetics were investigated in this investigation. In 1986, Derradji and Kassabji employed a plasma spray approach to create ZrN coatings for tool applications. [4] In 1987, Valikhani and Chandrashekhar examined the performance of ZrN and TiN coated twist drills, concluding that ZrN surpassed TiN in terms of service lifetime and drilling quality. Sue et al. investigated the erosion behaviour of ZrN coatings in 1988 [4] and 1990. In the following two decades, various studies on ZrN

coatings were conducted to evaluate their erosion protection for turbine and compressor blades, microhardness, adhesion, wear at 500–600 1C, biocompatibility, orientation dependence, Optical and electrical properties, tribology, nuclear fuel element compatibility, and composition and bonding.

The chemical and physical features of zirconium nitride make it a desirable material. ZrN films have often been used in hard coatings due to their outstanding mechanical qualities [5, 6]. ZrN thin films have attracted a lot of interest for a variety of applications, including wear-resistant coatings on steel drill bits, diffusion barriers in IC technology, cryogenic thermometers, hard coatings, protective coatings on steel vessels handling molten metal, and Josephson junctions as a solar energy collector surface film. The earliest experiments that surfaced on ZrN based temperature sensors was in 1987 in a study conducted by Tsutom Yotsuya et al. [7] [8]. In this study, A cryogenic temperature range thin-film thermometer was produced utilising sputtered Zr-N films. Zr-N thermometers offer a wide temperature range of sensitivity, from 300 to 2 K or even lower.

It was discovered that by altering deposition parameters such as substrate temperature, nitrogen partial pressure, and deposition rate, the temperature coefficient of electrical resistance (TCR) may be regulated. Furthermore, sputtered Zr-N films were projected to have a lower magnetoresistance than other semiconductor-type materials, making them appropriate for temperature sensors in high magnetic fields. It was possible to create stable resistance thermometers with low magnetoresistance, quick reaction, and a negative TCR for cryogenic temperature measurement.

This study aims to fabricate a Zirconium Nitride thin film using RF Magnetron Sputtering and obtain a thin film of thickness ranging between 200-300nm, with the lowest possible negetive TCR for application in temperature sensors suited for deep space application.

Chapter 2

Literature Review

The earliest experiments that surfaced on ZrN based temperature sensors was in 1987 in a study conducted by Tsutom Yotsuya *et al.* in his paper titled ," New type cryogenic thermometer using sputtered ZrN films" [8]. The author describes a novel type of thin-film thermometer using sputtered Zr-N films especially for cryogenic temperature. Zr-N thermometers were described to have high sensitivity in a wide temperature range from 300 to 2 K and a quick response. It was established that the temperature coefficient of resistance (TCR) of ZrN could be maintained by adjusting the deposition conditions of the thin film such as substrate temperature, nitrogen partial pressure, and deposition rate. The magnetoresistance of sputtered Zr-N films were also studied and found to be lesser than other semiconductor type materials, thus establishing these films as one suited for applications involving high magnetic fields. In this study, Zirconium nitride films were sputtered on sapphire substrates of 0.5 mm thickness using a conventional radio frequency (13.56 MHz) magnetron sputtering unit through a stainless-steel mask. A zirconium metal disk of 99.9% purity and a size of 100 mm diameter was used as a target. Reactive sputtering was performed using an argon and nitrogen medium. The partial pressure of nitrogen was varied from its initial value of 0.8 to 4 mTorr to control the TCR and the resistivity of the films, while the total pressure of the gas mixtures was allowed to remain constant at 6 mTorr. Since TCR was found to be profoundly affected by the nitrogen partial pressure, and since negative TCR was desirable for cryogenic thermometry, nitrogen partial pressures between 2 and 4 mTorr were chosen for deposition of Zr-N films. Incident power utilized for the process was set to 200 W and the sputtering

time was about 15 min for the film thickness of 200 nm. The resistance and TCR of the developed sensor were measured in the temperature range between 2 to 300 K. This was done in a cryostat where a calibrated germanium thermometer and a copper-constantan thermocouple were mounted close to the sample. The Zr-N sensor thus fabricated was found to have a sensitivity at room temperature with its value slightly smaller than that of the platinum thermometer and was found to be equivalent to carbon resistance thermometers at 4.2K. The author prescribes a thermal cycle test to check stability and the reliability of the Zr-N thermometer. The film resistance was found after every thermal cycle to be at 77K. After 50 cycles the resistance change is less than 0.023% which gives a maximum error of 0.07 K at 77 K. Thus it was concluded in the study that Zr-N thin-film thermometers were capable of the thermometry from 300 to 2 K. It was found to have a negative temperature coefficient of resistance and was found to be comparable to those of other types of resistance thermometer. High thermal stability was also observed at 77 K.

Tsutom Yotsuya, Masaaki Yoshitake and Takao Kodamat in their paper titled," Low-Temperature thermometer using sputtered ZrN thin film" [7]study the fabrication and the resultant responses of a zirconium nitride thin film thermometer for low temperature applications. The zirconium nitride thermometer was fabricated using the RF magnetron sputtering mechanism where a pure Zr plate was used as the target in a vacuum chamber 1×10^{-2} Torr with Ar and N_2 gas as the carrier and reactive gases. The target was placed at 50nm distance from the substrate and at an input RF power of 200W, the film of 200nm thickness was deposited by 15 mins. The effect of fabrication conditions on the film were studied by varying the partial pressure of nitrogen within the chamber. Using Auger Electron Spectroscopy, the different compositions of zirconium nitride and their resistances were studied. According to the studies conducted it was inferred that the deposition conditions such as rate of deposition, substrate temperature and the ratio of argon and nitrogen in the reactive gas mixture. To obtain the optimum ratio of Ar to Nitrogen, the films were produced at different N_2 partial pressures. The TCR and resistances were also studied at 273K

The first set of films developed were metallic Zr films with N_2 partial pressure below 0.3mTorr. The Zr thin film thus prepared exhibited metallic behaviour, having

low resistivity and a positive TCR. It was found that the resistance increased with the increase in N2 partial pressure, while the TCR decreased. The next film developed was with nitrogen partial pressure maintained around 0.5mTorr. the resultant film exhibited a golden colour and had smaller resistivity and large positive TCR. The next film generated was obtained keeping the nitrogen partial pressure greater than 0.8mTorr. here, the lattice structure was found to be disoriented due to excess nitrogen atoms in the film where, the film showed relatively large resistance and negative TCR. X-Ray Diffraction Analysis of the film generated showed that the crystal thus generated resembled that of amorphous structure. The author then discusses his results starting with the thermal cycles that was studied. For this the temperature dependence of resistance was studied for nitrogen partial pressures between 2.5 to 3.3mTorr. 2 different calibrated thermometers were employed as reference thermometers for the same. A calibrated Pt thermometer was used for temperatures above 60K and a calibrated Ge thermometer was employed for temperature below 60K. The thermometers showed a negative TCR. Both the resistance and the sensitivity were found to have increased with decreasing temperature. The films grown under an ambient substrate temperature were found to involve large stresses.

The resistance of the film was found to increase with each repeated thermal cycle. A drift in resistance was observed after each cycle and was caused by the thermal cycling. Though the value seemed to reduce, this phenomenon was to be eliminated. To eliminate this undesirable drift in resistance, the substrate temperature was elevated to 300°C. The electrode films were additionally evaporated at 300°C in 5×10^{-6} Torr. This process of annealing was useful to suppress the resistance drift. The sample thus prepared was thermally cycled 50 times between room temperature and 77 K. The temperature error at 77 K was found to be 17 mK for the treated sample. When the ZrN film was kept at a low temperature, such as 4.2 K, the resistance drift was not observed which concluded that the difference in the thermal expansion coefficients between ZrN and the substrate was the root cause causes the resistance drift. It was found that the sensitivity of a ZrN thermometer was similar to that of a Pt thermometer near room temperature and that of a carbon resister at 4.2 K. it was concluded that a ZrN film thermometer can determine temperature over a wide range and both the resistivity and TCR were found to increase with increasing N2 partial pressure

thus making it possible to obtain desirable sensitivity for any temperature range.

B.Subramanian *et al.* in the paper titled, "Reactive DC Magnetron Sputtered Zirconium Nitride (ZrN) Thin Film and its Characterization [9]", describe the preparation of Zirconium nitride (ZrN) thin films using reactive direct current (DC) magnetron sputtering onto different substrates. In this study, ZrN thin films were deposited on Mild steel (MS), Silicon wafer and glass using a 12" HINDHIVAC DC magnetron sputter deposition unit. The base vacuum of the chamber was maintained to be below 1×10^{-6} Torr at different substrate temperatures. High purity argon was used for the plasma generation process. The author employs Xray diffraction (XRD) to examine the changes in preferred grain orientation. XRD patterns were recorded using an X'pert pro diffractometer using Cu-K (1.541Å) radiation from a 40kV X-ray source running at 30 mA. The surface of the coating was characterized by the use of a molecular imaging Atomic Force Microscope. Micro hardness of the films on steel were evaluated by using a DM-400 micro hardness tester from LECO with Vickers indenters. Zirconium Nitride films were deposited by reactive DC magnetron sputtering technique on different substrates. The presence of polycrystalline with face centered cubic structure had been predictable from the x-ray diffraction phase analysis. The spherical granular morphology of ZrN hard coatings was observed from atomic force microscopy. It was confirmed that the ZrN hard coatings showed good optical quality from photo luminescence spectrum. Corrosion test was carried out in 3.5% NaCl solution by using potentio-dynamic polarization and electrochemical impedance spectroscopy.

The effect of variation in the ratios of Argon and Nitrogen were studied by Nicky P Patel *et al.* in the paper titled, "Characterization of sputtered zirconium nitride films deposited at various argon:nitrogen ratio" [10]. In this study, zirconium nitride thin films were deposited by reactive magnetron sputtering using argon as inert gas and nitrogen as reactive gas. Zirconium nitride coatings were deposited on corning glass substrates. For this, specially crafted chambers were utilized for reactive magnetron sputtering. The target material used was zirconium with 50.8mm diameter and a purity of 99.999%. The chamber was initially evacuated to a base pressure of 6x10-4 Pa, with the use of a turbo molecular pump backed up with a rotary pump. High

purity argon and nitrogen gas flow was allowed into the chamber and the flow of gas rate was controlled using a Mass Flow Controller. X-ray Diffractometer was preferred to analyse the structural properties of zirconium nitride thin films. The surface morphology of zirconium nitride thin films were studied using a scanning electron microscope and atomic force microscope. Optical properties of zirconium nitride thin films was finally analysed by a UV-Vis-NIR spectrophotometer.

The XRD patterns for zirconium nitride thin films were deposited such that the Ar:N2 gas ratio was varied with increments of 4 units each, such as, 20:20, 20:16, 20:12, 20:08, 20:04. When Ar:N2 ratio was 20:20, (011) peak of Zr_3N_4 having very low intensity was observed. A very low intensity peak (111) of Zr_3N_4 was also observed when nitrogen gas flow was 20 sccm. As the flow rate of nitrogen decreases to 16, 12 and 8sccm the intensity of the peak (011) increases subsequently. The (011) peak was found to exhibit maximum intensity at the least flow rate of nitrogen at 4sccm.

Thus it was observed that the decrease in Ar:N_2 gas ratio leads to highly intense (011) peak for zirconium nitride films. With an increase in the Ar:N2 gas ratio from 20:04 to 20:20, the average crystallite size of zirconium nitride films reduces from 9 to 7 nm. The average maximum transmittance for an Ar:N2 gas ratio at a 20:20 sccm was 82 percent..

P.J. Kelly and R.D Arnell, [11] in their study titled,"Magnetron sputtering: a review of recent developments and applications" describes the different developments in the field of magnetron sputtering. This paper discusses a number of advancements in the magnetron sputtering field. These include duplex surface engineering methods, pulsed magnetron sputtering, variable field strength magnetrons, and closed field unbalanced magnetron.

The author describes the various trends that has been imperative in sculpting the magnetron sputtering process. A target (or cathode) plate is bombarded by intense ions produced by discharge plasma that is located in front of the target in the initial introduction of the sputtering process. The bombardment results in sputtering, or the removal of target atoms, which then condenses as a thin layer on a substrate. The target surface's secondary electrons, which are produced as a result of the ion bombardment, are crucial to maintaining the plasma. Despite being widely employed, the technique was discovered to be constrained by slow deposition rates, poor plasma

ionisation efficiency, and significant substrate heating effects. To overcome these limitations, the more recent advancements such as magnetron sputtering and unbalanced magnetron sputtering were discussed.

Next, an unbalanced magnetron sputtering is introduced. Here, the outer ring of magnets is strengthened relative to the central pole. Thus, not all the field lines are closed between the central and outer poles in the magnetron. Instead some are directed towards the substrate, and some secondary electrons are able to follow these field lines. As a result, the plasma is free of being strongly confined to the target region. Thus, high ion currents were found to be extracted from the plasma without the actual need to externally bias the substrate.

Despite having its advantages, the unbalanced magnetron sputtering, was found to pose difficulty in uniformly coating complex components at acceptable rates from a single source. The commercial exploitation of this technology was introduced through multiple magnetron systems.

The magnetic arrays in nearby magnetrons in a multiple magnetron system were set up with either the same or the opposite magnetic polarity. The configuration was described as mirrored in the first instance and as a closed field in the second. The field lines in the mirrored casing were pointed at the chamber walls. Low plasma density was observed in the substrate region as a result of the loss of secondary electrons that followed these lines. The field lines were connected between the magnetrons in the closed field configuration.. The Losses to the chamber walls were low and the substrate was found to be in a high density plasma region. Thus the developments discussed were found to have transformed the capabilities of magnetron sputtering, and helped to establish it as the process of choice for the production of many industrially important coating/substrate systems.

In the paper titled, "Effect of deposition temperature on microstructure and corrosion resistance of ZrN thin films deposited by DC reactive magnetron sputtering", authored by Daiane Roman *et al.* thin films of zirconium nitride were fabricated using direct current reactive magnetron sputtering on different substrates, and the parameters such as the deposition time, Ar/N2 partial pressure ratio and substrate temperature were varied. This study was conducted with an aim to understand the

physicochemical, crystalline structure and corrosion resistance of the thin films thus created using glancing angle X-ray diffraction, Rutherford backscattering spectrometry, scanning electron microscopy, X-ray photoelectron spectroscopy and potentiodynamic polarization tests.

For the preparation and characterization the ZrN films, three different substrates were utilized, namely, C (graphite), Si(1 0 0) wafer and Ti respectively. Different substrates were used due to the effect that each one of the substrates had over the results of different characterization techniques. The silicon substrate was utilized as a flat surface where the ZrN thin film can be deposited avoiding the effects of a rough surface. Similarly, such a substrate eliminated the need of any cutting or polishing processes. Another advantage was that in SEM analysis it was easy to cleave the structure. Thus the Si substrate was utilized for XRD and SEM analysis.

Because of its properties as a biomaterial, the Ti substrate was chosen for corrosion experiments. The Ti samples were ground after being sliced into different sizes, and they were then polished with an alumina suspension containing particles that could reach a size of 0.1 m. After that, the samples were cleaned for 30 minutes in an ultrasonic bath with acetone. The films were deposited simultaneously on the different substrates by DC reactive magnetron sputtering from a Zr target in Ar/N_2 plasma, with a total pressure of 2×10^{-2} mbar and a power of 100W at the target. The base pressure maintained in the chamber was 1×10^{-7} mbar. As a result three sets of samples were produced. In the first case the partial pressure of N_2 ranged from 0.2×10^3 to 1.7×10^2 mbar. In the second case the deposition time was varied from 10 to 80 min. In the third case the substrate temperature was varied from 25 to 500 ◦C.

Corrosion tests were performed in a VoltaLab model PGZ100 potentiostat/galvanostat at 37°C in non-deaerated solutions. The electrolyte used was AFNOR S90-701, an artificial saliva solution made using analytical-grade chemicals without any prior purification. The working electrode was a titanium substrate with a circular geometry that was either ZrN-coated or untreated. The thin film area that was to be investigated for the corrosion tests was established by partially encasing the sample in insulating resin. The sample was exposed to the electrolytic solution over a 0.95 cm2 region. The working electrode was cleaned with ethanol, degreased with acetone,

and rinsed with distilled and deionized water prior to each experiment. As the reference electrode, a saturated calomel electrode (SCE) was connected, and the auxiliary electrode used was a graphite rod.

The author thus concludes that the film thickness increases when the N_2 partial pressure decreases and alongside, its deposition time also varies proportionately. When the size of the resulting film is relatively thin, no preferred orientation is shown by the film's microstructure. When the resulting film is relatively thick, there is a preferred orientation in the (1 1 1) direction as shown by the XRD results. XPS results were found to reveal the presence of ZrN but also oxide and oxynitri dephases attributed to the air exposure after the deposition process. The corrosion behavior was evaluated by potentio-dynamic polarization experiments in artificial saliva. The deposition temperature and the oxidation of the surface were found to play an important roles in the corrosion behavior. For relatively high deposition temperatures, the exposure of the thin ZrN films to the atmosphere would leads to the undesirable formation of the oxides and oxynitrides at the surface and the pitting corrosion resistance is found to be increased.

. Jiménez *et al.* in their study titled. "Effect of the substrate temperature in ZrN coatings grown by the pulsed arc technique studied by XRD [5]" dwells deeper into the effect of varying substrate temperature. The experimental process described consists of a vacuum system, which includes a reaction chamber incorporating two opposing electrodes. The cathode is composed of a zirconium disc with 99.99% of purity and the anode is the substrate.

A high power supply was utilized to generate pulses to produce the discharge between the electrodes.A vacuum of 1×10^{-5} mbar was generated in the chamber.In order to control the number of pulses, the discharge voltage, and the active and passive periods of each pulse, ZrN films were produced with three pulses using nitrogen as the working gas at a pressure of 3mbar and a voltage of 270V. The discharge voltage between the electrodes amounts to 270V during the active phase, and it is zero during the passive time of the pulse. This generates a discharge like a square wave. The coatings were grown at 1 s as passive and active time.

It was concluded that the plasma aided repeated pulsed arc technique was used to grow ZrN films, and different Ts at 50 °C, 100 °C, 140 °C, 170 °C, 200 °C, 230 °C,

and 260 °C were using SPM and XRD.The (200) plane's crystallographic texture is visible at low Ts is often less than the one at temperatures above 200 °C is regarded as the changeover temperature.Despite not having the thickest films, samples produced at 200 °C showed the maximum intensity of the (200) plane. When T_s is below 200 °C, the microstress drops as a function, but once T_s is above 200 °C, it is nearly constant. indicating that 200 °C is a crucial temperature; when it is exceeded, the properties of the formed films would change. Grain size was found to initially increase with thickness, but this relationship has a limit. The strain energy increased as the thickness increases, which was bound to result in additional flaws. These flaws may serve as fresh nucleation locations, renewing competition between the existing older grains, thus decreasing the grain size.

Chapter 3

Fabrication and Characterization ZrN Thin Film

The entire process of sensor fabrication consists of a series of steps of which the fabrication of the thin film is one of the most important. Different methods have been employed to develop the ZrN thin film. These include Chemical Vapor Deposition (CVD), Physical Vapor Deposition (PVD), Cathodic Arc Deposition, Plasma Spray, Ion Beam Implantation and Pulsed Laser Deposition Of these methods, the one used in this study is RF Magnetron Sputtering.

3.1 Thin Film Deposition and Characterization

Figure 3.1 shows the magnetron sputtering technique in action. It is a physical vapour deposition technique that includes transferring materials from a target source to the substrate's surface. Only a small portion of the particles that are released from the target during sputtering get ionised, despite having an energy of up to 100 000 kV. The ions that have been energized shoot in straight lines and impinge onto the substrate, causing the re-emission of the already deposited materials from the surface of the substrate, *i.e.* re-sputtering. Allowing ions from the target to collide with gaseous atoms at high pressure is another method for achieving sputtering. As a result, the ions' velocity is moderated, leading them to diffuse in the direction of the substrate and condense on its surface. In the gaseous case, the impact energy of the ions is dependent on the gas pressure and is modifiable by altering the former. The

common gases employed have an atomic weight close to that of the target and are inert. Amongst the reported sputtering methods are RF reactive magnetic sputtering, [12] DC/RF reactive magnetron sputtering, [13] DC reactive magnetron sputtering, [14,15] ion beam sputtering, [16] and dual ion beam sputtering. [17]

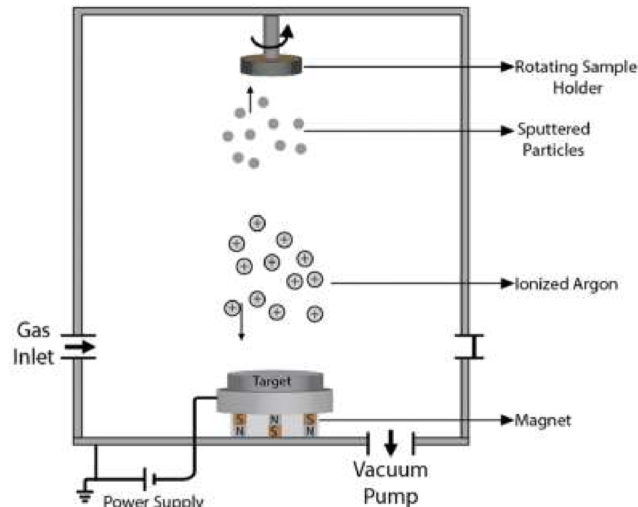

Figure 3.1: Schematic Illustration of Magnetron Sputtering Method

The RF Magnetron Sputtering unit is composed of a chamber in which the heating arrangement is installed. it consists of a shutter and the target is mounted within. The ceramic or sapphire substrate is mounted within the chamber with a constant heat load applied to it and evacuated. Evacuation is done with the help of a rotary pump to a vaccum pressure of 1×10^{-2}mbar. Following this, the diffusion pump is used to evacuate once more to improve the vaccum pressure within the chamber to 10^{-5} mbar.

The target for the study is high purity Zirconium, which is mounted onto the top of the unit, within the chamber. Similarly, on the base plate, the ceramic substrate is mounted. The target is provided with a negative voltage whereas the substrate is at ground potential. Due to this potential difference, the zirconium metal ions are emitted from the surface of the target and deposit themselves over the substrate. Thus the process of deposition occurs in Ar atmosphere. The Ar-N_2 concentrations are varied using a Mass Flow Controller. The presence of a magnetic field in the target ensures that the sputtered ions are concentrated onto the focused substrate alone. Figure 3.2 shows the sputtering unit used for thin film deposition and Figure 3.3 represents the Mass Flow Controllers. The mass flow controller is set for N_2 and

the value of K factor is included in the calibration conversion. A relative K factor is used to relate the calibration of the actual gas to the reference gas as Ar, whose k factor is 1.4573 with respect to N_2 using the equation,

$$K = \frac{Q_a}{Q_r} = \frac{K_a}{K_r}$$

where, Q_a = mass flow rate of an actual gas (sccm)

Q_r = mass flow rate of a reference gas (sccm)

K_a = K factor of an actual gas

K_r = K factor of a reference gas

Figure 3.2: RF Magnetron sputtering equipment

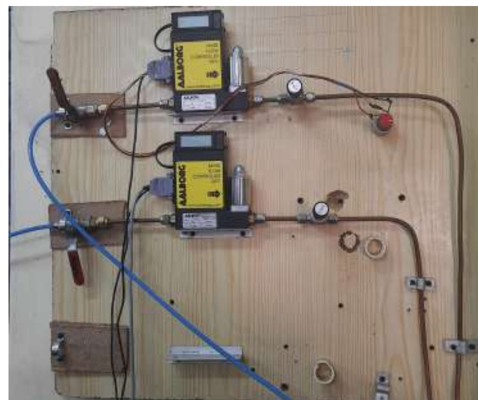

Figure 3.3: Mass Flow Controller

After the fabrication process is completed, the sample of required thickness is cut using precise cutting tools, from the substrate after being characterized in order to

understand their surface morphology and thickness etc. This process is followed by the process of drawing electrodes. Silver electrodes have been used for this sensor. These electrical contacts can be printed onto the sensor or electrical contacts can be drawn manually. In the latter technique a bare wire is wound around the sensor and silver paste is used to create the electrical contacts. Once electrodes are added onto the fabricated module, the sensor is then isolated and placed in a decicator for 24 hours and insulated using Teflon. This is followed the outer casings and insulations, which consists of the copper quarter inch tube sealed on either ends by the use of M-seal. After making the entire sensor, the next step of sensor manufacturing would be thermal cycling, where the reliability of the sensor is tested by measuring the resistance at room temperature and after being exposed to low temperatures. If the sensor shows the same values at both the extremities, in consequent cycles, then it is deemed viable for use. such a viable sensor is then taken for caliberation using a cryostat. In this study we have utilized an experimental cryostat which is a Two-stage GM Cryo-cooler.(Figure 3.3)

Figure 3.4: Two-stage GM Cryo-cooler

The thin film which is developed is then mounted onto the thermal block of the cryo-cooler. The thermal block initially goes to the value corresponding to the room temperature and then reduce to values between 10 and 12K thus simulating the cryogenic temperature ranges. Since the cryo-cooler is connected with a data accuisition system in which we compare the measuremnts of 2 commonly available sensors, namely Si and Pt sensors. From the data accuisition system, the values of voltages with respect to the change in temperature is obtained.

Chapter 4

Results

4.1 Obtaining the Sample Thickness

The process of sputtering of ZrN over the ceramic substrate was done at different time intervals. This was done with the aim that we obtain a sample with a thickness ranging between 200 to 300nm. On taking the various samples, it was found that in the sample that underwent sputtering for a duration of 30 minutes showed the desired thickness.Thin film X-ray Diffraction was used to study the thickness of the sample. The thin film with the desired thickness was then taken into account for further study.

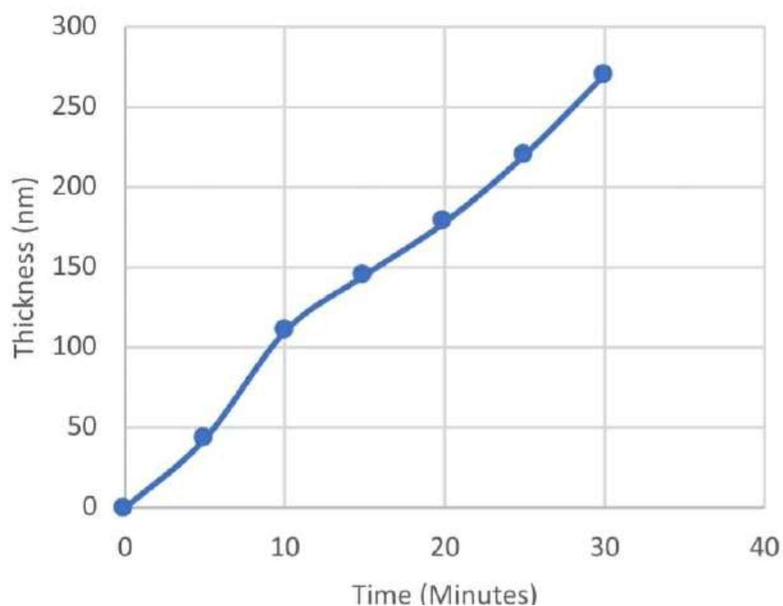

Figure 4.1: Variation in Thickness of ZrN Thin Film with Temperature

4.2 Obtaining the Lowest Negetive Temperature Coefficient

The next objective of the work was to identify the possible negetive temperature coefficients for varying Ar-N_2 partial pressures. For this the concentration of the argon and the nitrogen gases were controlled in three cases using the mass flow controller. For this, the Deposition pressure was maintained at 8×10^{-3}mbar. The input power to the sputtering unit was maintained at 200W. The Argon partial pressure was also maintained at 8×10^{-3}mbar. Thus keeping the duration of sputtering constant at 30 minutes, the nitrogen partial pressure was varied. The resultant film is then analysed and its resistance is measured to calculate the temperature coefficient using the formulae TCR = $(\mathrm{R}_2 - R_1) \times \frac{1}{R_2(T_2-T_1)}, where,R_2$ stands for the resistance at room temperature and R_1 is the resistance at low temperatures. Here, (T_2-T_1) are the temperature difference.

4.2.1 N_2 Partial Pressure at 2×10^{-3}mbar.

In the first case, the value of Nitrogen partial pressure is maintained at 2×10^{-3}mbar. The resistance measured at room temperature was 3.5KΩ.

The value of TCR is calculated as -(1.72×10^{-3}.)

$$TCR = (R_2 - R_1) \times \frac{1}{R_2(T_2 - T_1)}$$

$$= (3.53K - 5.94K) \times \frac{1}{5.94(280.9 - 45.5)}$$

$$= -1.75 \times 10^{-3}$$

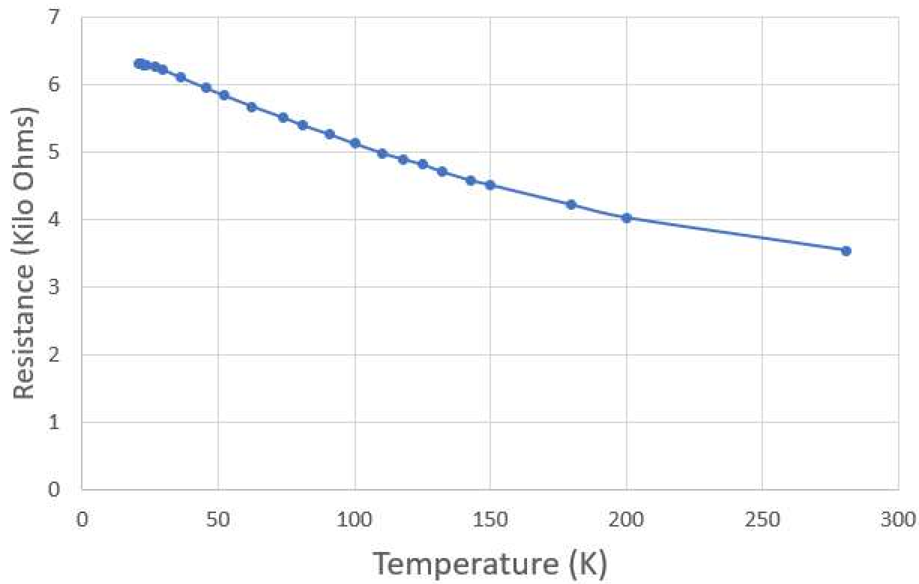

Figure 4.2: Variation in resistance of ZrN thin film with temperature at N2 partial pressure of 2×10^{-3}mbar

4.2.2 N_2 Partial Pressure at 2.5×10^{-3}mbar.

In the second case, the value of Nitrogen partial pressure is maintained at 2.5×10^{-3}mbar. The resistance measured at room temperature was 6.46KΩ.

The value of TCR is calculated as -(3.09×10^{-3}.)

$$TCR = (R_2 - R_1) \times \frac{1}{R_2(T_2 - T_1)}$$

$$= (6.49K - 26.2K) \times \frac{1}{26.2(287.2 - 44.1)}$$

$$= = 3.09 \times 10^{-3}$$

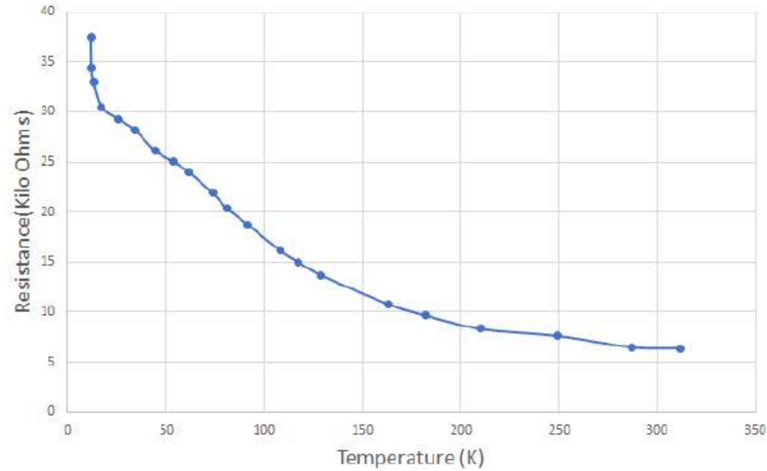

Figure 4.3: Variation in resistance of ZrN thin film with temperature at N2 partial pressure of 2.5×10^{-3}mbar

4.2.3 N_2 Partial Pressure at 3×10^{-3}mbar.

In the final case, the value of Nitrogen partial pressure is maintained at 3×10^{-3}mbar. The resistance measured at room temperature was $41K\Omega$.

The value of TCR is calculated as -(3.26×10^{-3}.)

$$TCR = (R_2 - R_1) \times \frac{1}{R_2(T_2 - T_1)}$$

$$= (41.1K - 221.3K) \times \frac{1}{221.3(295 - 45.2)}$$

$$= -3.26 \times 10^{-3}$$

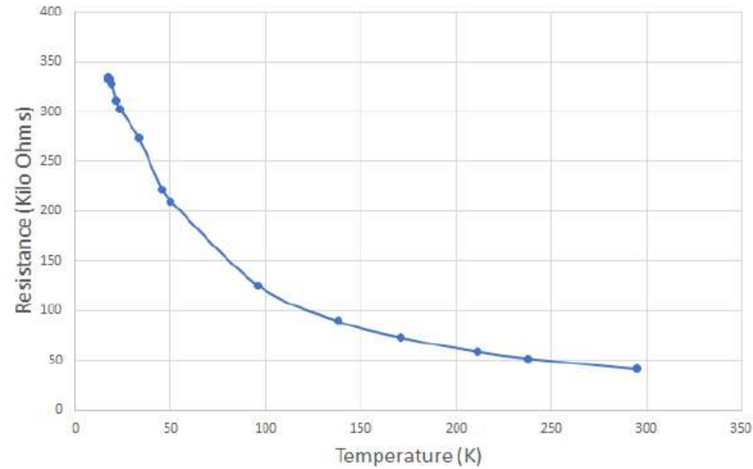

Figure 4.4: Variation in resistance of ZrN thin film with temperature at N2 partial pressure of 3×10^{-3}mbar

Table 4.1: Comparison of NTCR at different partial pressures of N_2 .

N_2 Partial Pressure (mbar)	Negetive Temperature Coefficient of Resistance NTCR (K^{-1})
2×10^{-3}	-1.75×10^{-3}
2.5×10^{-3}	-3.09×10^{-3}
3×10^{-3}	-3.26×10^{-3}

We find that out of the three cases, the lowest negetive temperature coefficient has been exhibited by the sample fabricated at Nitrogen partial pressure, 3×10^{-3}mbar. Thus we choose this case as our most desireable thin film.

4.3 Comparison of ZrN Thin Film Generated with Si and Pt RTD

Silicon and Platinum diodes are the two types of most commonly used temperature sensors. Platinum diode are suitable for measuring high temperatures while Silicon diode offers a moderate performance over the entire temperature range.On using the cryostat for comparison, the data accusition system collects the resistance variation of the three kinds of sensors. With these two sensors, we compare the functionality of our ZrN thin film. Figure 4.4 shows that among the three, Pt sensors exhibit

a positive temperature coefficient unsuited for cryogenic applications. At the same time, it can be identified that ZrN shows a superior Negetive TCR thus concluding ZrN thin films are found suitable for measuring low temperatures especially in the cryogenic temperature range.

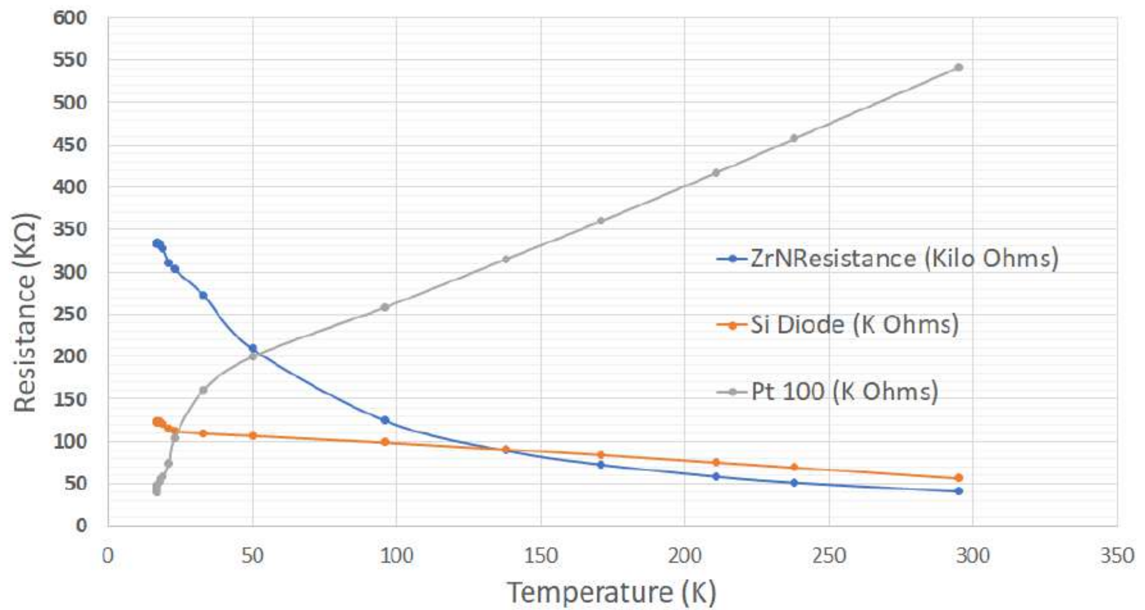

Figure 4.5: Variation in resistance with temperature of Platinum RTD, Silicon RTD, and ZrN Thin Film.

Table 4.2: Variation in resistance with temperature ZrN Thin Film Silicon and Platinum Resistance Temperature Detectors.

Resistance in kilo-ohms			
Temperature (K)	ZrN	Si Diode	Pt 100
295	41.1824	57.0037	541.684
238	51.89	69.71	248
211	58.85	75.7	417.47
171	72.92	84.43	360.28
138	89.4	91.06	315.32
96	124.8	99.19	258.43
50	209.6	107.09	199.96
33	272.9	109.76	160.97
23	303	112.5	104.55
21	311.3	115.6	74.43
19	327.6	120.7	57.96
18	331	122.6	55.83
18	332.8	123.2	52.85
17	333.7	123.3	49.19

Chapter 5

Conclusion

Among the various application of ZrN hard coatings, cryogenic temperature measurement is one of the most important. Due to its many different physical properties, ZrN is widely used in hostile environments. Thus we used RF magnetron sputtering mechanism to fabricate a thin film of ZrN over a ceramic substrate.

The deposition conditions that largely affect the structure and properties of coatings include the coating composition, reactive gas flow rate, substrate bias and temperature. In the study, we have successfully been able to fabricate a thin film of ZrN such that the desired film thickness of 200-300nm is obtained. following this, the nitrogen partial pressures were varied in three graditions namely, 2×10^{-3}mbar, 2.5×10^{-3}mbar and 3×10^{-3}mbar. Out of these, the three variations, on calculating the NTCR, we identify that the lowest negetive temperature coefficient is obtained at the nitrogen partial pressure of 3×10^{-3}mbar. This ZrN thin film is then developed and compared with the existing Silicon and Platinum sensors and it was inferred that the ZrN thin film thus developed is more suited for cryogenic applications.

References

[1] A. Ul-Hamid, "The effect of deposition conditions on the properties of zr-carbide, zr-nitride and zr-carbonitride coatings–a review," *Materials Advances*, vol. 1, no. 5, pp. 988–1011, 2020.

[2] K. Sugiyama, K. Watanabe, S. Motojima, and Y. Takahashi, "Single crystal growth of zirconium nitride by modified filament-method," *Bulletin of the Chemical Society of Japan*, vol. 52, no. 2, pp. 420–424, 1979.

[3] A. Zabolotskii, S. Salibekov, I. Kantsevich, N. Ignatova, and A. Chernyak, "Reaction between carbon fibers and nickel through a zirconium nitride or titanium carbide diffusion barrier," *Soviet Powder Metallurgy and Metal Ceramics*, vol. 16, no. 7, pp. 519–521, 1977.

[4] J. A. Sue and H. H. Troue, "Zirconium nitride coated article and method for making same," Jun. 9 1992, cA Patent App. 000,547,766 A.

[5] H. Jiménez, E. Restrepo, and A. Devia, "Effect of the substrate temperature in zrn coatings grown by the pulsed arc technique studied by xrd," *Surface and Coatings Technology*, vol. 201, no. 3-4, pp. 1594–1601, 2006.

[6] H. J. Ramos and N. B. Valmoria, "Thin-film deposition of zrn using a plasma sputter-type negative ion source," *Vacuum*, vol. 73, no. 3-4, pp. 549–554, 2004.

[7] T. Yotsuya, M. Yoshitake, and T. Kodama, "Low-temperature thermometer using sputtered zrnx thin film," *Cryogenics*, vol. 37, no. 12, pp. 817–822, 1997.

[8] T. Yotsuya, M. Yoshitake, and J. Yamamoto, "New type cryogenic thermometer using sputtered zr-n films," *Applied physics letters*, vol. 51, no. 4, pp. 235–237, 1987.

[9] B. Subramanian, K. Ashok, C. Sanjeeviraja, P. Kuppusami, and M. Jayachandran, "Reactive dc magnetron sputtered zirconium nitride (zrn) thin film and its characterization," in *Journal of Physics: Conference Series*, vol. 114, no. 1. IOP Publishing, 2008, p. 012039.

[10] N. P. Patel, K. V. Chauhan, J. M. Kapopara, N. N. Jariwala, and S. K. Rawal, "Characterization of sputtered zirconium nitride films deposited at various argon: nitrogen ratio," in *IOP Conference Series: Materials Science and Engineering*, vol. 149, no. 1. IOP Publishing, 2016, p. 012015.

[11] P. J. Kelly and R. D. Arnell, "Magnetron sputtering: a review of recent developments and applications," *Vacuum*, vol. 56, no. 3, pp. 159–172, 2000.

[12] C.-H. Lai, M.-H. Tsai, S.-J. Lin, and J.-W. Yeh, "Influence of substrate temperature on structure and mechanical, properties of multi-element (alcrtatizr) n coatings," *Surface and Coatings Technology*, vol. 201, no. 16-17, pp. 6993–6998, 2007.

[13] P. Dubey, V. Arya, S. Srivastava, D. Singh, and R. Chandra, "Effect of nitrogen flow rate on structural and mechanical properties of zirconium tungsten nitride (zr–w–n) coatings deposited by magnetron sputtering," *Surface and Coatings Technology*, vol. 236, pp. 182–187, 2013.

[14] E. Silva, M. R. de Figueiredo, R. Franz, R. E. Galindo, C. Palacio, A. Espinosa, C. Mitterer, S. Carvalho *et al.*, "Structure–property relations in zrcn coatings for tribological applications," *Surface and Coatings Technology*, vol. 205, no. 7, pp. 2134–2141, 2010.

[15] M. Balaceanu, T. Petreus, V. Braic, C. Zoita, A. Vladescu, C. Cotrutz, and M. Braic, "Characterization of zr-based hard coatings for medical implant applications," *Surface and Coatings Technology*, vol. 204, no. 12-13, pp. 2046–2050, 2010.

[16] M. Larijani, M. Zanjanbar, and A. Majdabadi, "The effect of carbon fraction in zr (c, n) films on the nano-structural properties and hardness," *Journal of alloys and compounds*, vol. 492, no. 1-2, pp. 735–738, 2010.

[17] G. Abadias, F. Pailloux, and S. Dub, "Epitaxial growth and mechanical properties of (001) zrn/w nanolaminates," *Surface and Coatings Technology*, vol. 202, no. 15, pp. 3683–3687, 2008.