A REVIEW ON SPUTTERED ZIRCONIUM BASED THIN FILMS

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Abstract – *Depending on properties required various forms of synthesis methods are used for coating a material on substrate. Zirconium has several unique properties such as good corrosion resistance, high hardness, high abrasive wear resistance and good low friction properties. In this paper we have summarized different physical methods through which thin films can be coated on a substrate and how the coating parameters affect the properties of thin films. Various properties such as Hardness, Optical Properties, Structural Properties, Wettability, Electrical resistivity, etc. are noted in this paper. This paper would be fruitful to those who want to have knowledge regarding physical deposition technique and their relative properties on the substrate.*

***Key Words*: Zirconium oxy-nitride, RF Magnetron, DC Magnetron, Hydrophobicity, Wettability.**

1. INTRODUCTION

Transfiguration metal oxynitride film, particularly zirconium oxynitride (ZrON), had pulled in extensive interests over the most recent couple of years because of their wonderful properties. ZrOxNy thin films had been broadly applied in gate dielectrics, temperature sensor component in attractive fields up to 32 T working at temperatures somewhere in the range of 2 and 286 K, corrosion resistance coatings, and decorative films**[1]**. Zirconium compound and composites of its oxides and nitrides are of extraordinary enthusiasm for some, application fields. Zirconium oxynitrides synthesis was reported by Gilles et al. Detailed examinations on the nitridation of zirconia have been displayed by Cheng and Thompson **[2]**. The strategies for generation of Zr oxynitrides depend on the controlled oxidation of zirconium nitride [6] or the nitriding of zir-conia, which requires high temperatures so as to embed nitrogen into the ZrO2 crystalline structure [1,2,10]. Specifically, oxynitride thin film can be kept utilizing RF receptive magnetron sputtering.

The present paper aim for determining the impact of the sub-strate temperature during deposition temperature on the crystalline structure and morphology of zirconium oxynitride thin films developed utilizing RF magnetron sputtering on AISI 304 hardened steel. **[3]**

2. Literature Review

Atuchin *et al.* (2013) Refer his article ZrON/Si (100) layer structure arrangement has been created by oxidation/nitrite at particle of sputtered Zr metal in n_2o/ar ambient at 500–900 1c. Micro morphology and basic properties of the films have been evaluate by examining electron microscopy, atomic force microscopy, and re-flection high-vitality electron diffraction. Dispersive optical properties of the ZrON/Si reflection framework have been examined with spectroscopic ellipsometry. An intense increment of sio2-based interface layer thickness has been found at 700– 900 1c. **[4]**

Balaceanu *et al.* (2008) State in his article results on the deposition and characterization of TiO_XN_Y/ZrO_XN_Y multilayers, with bilayer times of 20 and 400 nm, are exhibited. The coatings were kept on TiNiNb alloy substrates by the pulsed magnetron sputtering technique. The basic composition, hardness, adhesion and corrosion resistance of the coatings were investigated. As result of the XPS examination, the individual layers consisted of a mixture of titanium or zirconium oxinitrides and corresponding oxides. Just slight contrasts between the smaller scale hardness and bond estimations of the coatings with little and expansive bilayer period λ were found. The examinations also demonstrated that the multilayered coatings improved the erosion obstruction of the uncoated combination and reduced the measure of particle discharge in artificial body liquids.**[5]**

Carvalho *et al.* (2006) in this paper he investigate on ZrO_XN_Y thin films, the synthesis development with changing growth conditions and its connection with the structural and morphological properties of the films. The films were set up by RF responsive magnetron sputtering, utilizing different reactive gas streams. Composition and structure were measured by combining ion beam analysis (IBA) and x-ray diffraction (XRD) methods. The depth profiles of nitrogen and oxygen have been acquired by elastic recoil discovery investigation (ERDA). Results demonstrated that the oxygen portion in the films increments with gas stream, achieving an estimation of x-0.33 for a reactive gas flow mixture of 6.25 sccm. During growth mixed zirconium nitride and oxide phase form.**[6]**

Chen *et al.* (2013) Studied in his article thin films of zirconium oxynitride (ZrO_XN_Y) were deposited onto glass and Si substrate at room temperature by separated catholic vacuum arc (FCVA) technology utilizing air as a reactive gas. The composition and structures of the zirconium oxinitride films affected via air flow rate were explored by scan electronic spectroscopes, x-ray diffraction and x-ray photo electron spectroscopes. The result shows crystal structure of the film changed from ZrO and ZrN mixed stages to ZrN stage with the increasing air flow rate. The hardness, elastic modulus and flexible recovery parameter (ERP) of the zirconium Oxynitride films were additionally controlled by Nano space tests. The optical band gap of the film at the optimum deposition parameter was 1.91 eV, implying that the film had extraordinary possibilities in numerous photocatalytic and optoelectronic applications.**[7]**

Cubilios *et al.* (2016) State in his article morphological and basic changes of zirconium nitride and oxynitride thin film (ZrOxNy/ZrN) deposited via dc magnetron sputtering on stainless steel substrates (AISI 316l, 304ls, and 2205) in are active n2 and n2/o2 atmosphere mixed with argon were investigated. The crystallographic structures of the films were set up through x-ray diffraction (XRD). The morphology was evaluated by means of scanning electron microscopy (SEM) and atomic power microscopy (AFM), and the corrosion resistance was assessed utilizing electrochemical methods dependent on linear polarization (Pl). The XRD investigation demonstrated that the films were composed of cubic ZrOxNy and monoclinic ZrO_2. **[8]**

Pinzon *et al.* (2014). Refer his article the impact of the variation of electrical power applied to the objective on the morphology and optical properties of zirconium oxynitride - zirconium oxide (ZrON) films deposited via RF magnetron sputtering on regular glass substrates in a reactive atmosphere of N_2/O_2, with a stream proportion $\Phi N_2/\Phi O_2$ of 1.25 was explored. The crystallographic Structure of the films was set up through x-ray diffraction (XRD). The XRD examination showed that the films developed with mixed crystalline structures: monoclinic (ZrO2) and body-focused cubic (Zr2ON2). SEM examination showed that the films developed with a homogeneous morphology, and AFM results set up that as the electrical power applied to the objective increased, there were changes in the grain size and the roughness of the film. **[9]**

Guo *et al.* (2015) State in his article zirconium oxynitride thin film thermometers were shown to be valuable temperature sensors. Be that as it may, the fundamental conduction component of zirconium oxynitride films has been a long-standing issue, which upsets the expectation and improvement of their ultimate performance. In the low temperatures Range, while Mott variable bouncing conduction (VRH) was ruled the transport for films with generally low resistance, a crossover from Mott VRH conduction to Efros-Shklovskii (ES) VRH was observed for films with moderately high opposition. This low temperature crossover from Mott to ES VRH demonstrates the nearness of a coulomb gap (~ 7meV). **[10]**

Sr. No.	**Researchers**	**Substrate & Film**	**Coating parameters**	**Results**
1	**Cubillos *et al.*** (2013)	Stainless steel (Zr_2ON_2(AISI-316))	Temp. (287 K) -Diameter 1 m -Length 80 cm -Flow ratio (3) -Time 30 min -Band gap (1.8eV-3.3eV) -Power (~340 W) -XPS power (120 W)	XRD (2θ = 21°) -Deposition time (< 10 min) -Roughness (20.2mm) -Particle size (150-208 µm)
2	**Olaya *et al.*** (2014)	Stainless steel (Zr_2ON_2(AISI-304))	Working pressure ($7.4*10^{-1}$ Pa) -Target distance (5cm) -Time 30 min -Flow ratio (1.25) -Power (350W) -Temp (287-673 K)	XRD (2Ɵ = 28.3 at 287 K) (2Ɵ = 28.1 at 573 K) -Crystal size (32.1, 16, 18.5)nm -Thickness (256 nm) -Roughness (7.41 Å,31.7 Å,42.5 Å)
3	**Rizzo *et al.*** (2012)	Si ($ZrON_2$)	-sputtering pressure ($6*10^{-5}$Pa) -N_2 atm(1.86 pa) -partial pressure (0.01 Pa)	-Band gap (2.2-3.1 eV) -optical range (3.3-3.5 eV) -bending energy high (395 eV (ZrN_2))
4	**Song *et al.*** (2013)	Glass (ZrON)	-Size: 1.5*1.5 cm^2 -Base Pressure: $5*10^{-7}$ Torr -Power: 30 W -Time: 30 min -Ar:N_2(1:1) : flow rate: 16 sccm	-Film thickness: 20-50 nm -Transmittance: 20-60% -Wavelength: 300-350 nm
5	**Ferreira *et al.*** (2006)	Si (Zr_2ON_2)	-DC Power intensity: 100 $A\text{-}m^{-2}$ -Target distance :70 mm -Gas flow	-Film thickness: 5.2±0.2 µm Grain size: 3-11 nm -density of

			rate: 55 sccm -Working pressure: 0.4 Pa -Reactive gas floe rate: 5.5-16 sccm	defects: 125.18-73.16 mm^{-2}

Huang *et al.* (2007) Studied in his article the ideal deposition condition of ZrN thin film from our past investigation, by varying oxygen flow rate ranging from 0 to 8 sccm, monocrystalline ZrNxOy thin films were kept on p-type (100) Si substrates utilizing hollow cathode discharge ion plating (HCD-IP) system. The objective of this examination was to research the impact of oxygen content on the composition, structure and properties of the ZrNxOy thin films Phase separation of ZrNxOy to ZrN and monoclinic ZrO2 was found from X-ray diffraction (XRD) designs when the oxygen content was higher than 9.7 at.%. The hardness of the film marginally expanded as the oxygen content was under 9.7% and afterward decreased to 15.7 GPa, a typical hardness of ZrO2 stage, as the oxygen content additionally increased. The absolute pressure was near the worry in ZrN stage as the ZrO2 part was under 30%, and was near that in ZrO2 stage as the ZrO2 division was over 30%. **[11]**

Liu *et al* (2007) Refer his article a noble-metal-free elecrocatalyst dependent on carbon-supported zirconium Oxynitride (ZrOxNy/C) was set up by ammonolysis of carbon-supported zirconia (ZrO2/C) at 950◦C and examined as cathode elecrocatalyst towards oxygen decrease response (ORR) in PEMFCs. The elecrocatalyst was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM) procedures. The ZrOxNy/C elecrocatalyst introduced attractive catalytic activity for ORR. The beginning capability of ZrOxNy/C elecrocatalyst for oxygen decrease was 0.7V versus RHE and the four-electron pathway for the ORR was accomplished on the surface of ZrOxNy/C elecrocatalyst. The ZrOxNy/C elecrocatalyst demonstrated a similarly good cell execution to ORR in PEMFCs, particularly when worked at a relatively high temperature. **[12]**

Liu *et al.*(2009). State in his article a nanocrystal line ZrNxOy thin film was deposited utilizing hollow cathode discharge ion plating (HCDIP). ZrO2 and ZrN phase were distinguished by X-ray diffraction in the as-deposited film, recommending phase separation during the growth procedure. Since the crystallographic introductions of the ZrO2 and ZrN stages are arbitrary, the microstructure of the isolated phase is investigated with multiple central dark-field (MCDF) method. The compositional distribution between the isolated stages is investigated with Nano-ray energy dispersive X-ray spectroscopy (EDX). The results showed that zirconium oxynitride (ZrNxOy) thin film has a columnar structure with a substitute arrangement of ZrN and ZrO2, showing that oxygen molecules are inter-columnarly isolated segregated with a lateral diffusion distance lower than 20 nm. **[13]**

Moura *et al.* (2006) Refer his article spectroscopy has been utilized as a nearby test to characterized the structure evolution of magnetron-sputtered enriching zirconium oxynitride ZrOxNy films which result from an increase of reactive gas stream in the testimony. The deposited zirconium nitride film gives a Raman spectrum with the normal widened groups, due to the disorder induced by N vacancies. The recorded Raman spectrum of the zirconium oxide film is common of the monoclinic period of ZrO_2, which is uncovered likewise by X-ray diffraction. Raman spectra of zirconium oxynitride thin films present changes, which are observed to be firmly related with the oxygen content in films and the consequent basic changes. **[14]**

Porthinah *et al.* (2008) Studied his article in this work we produce $Zr_YO_XN_{1-X}$ thin coatings and $Zr_YO_XN_{1-X}$ by DC reactive magnetron sputtering. So as to examine the impact of nitrogen flow rates on physical and mechanical properties, the N_2/O_2 connection was changed somewhere in the range of 0.025 and 0.2. The increased of nitrogen to the ZrO_2 and $ZrO_2Y_2O_3$ frameworks was performed to think about the impact on the adjustment of the high temperature tetragonal or cubic periods of ZrO_2. The surface micro topography was investigated by Atomic Force Microscopy (AFM) and the roughness was evaluated. Scanning Electron Microscopy (SEM) was utilized to measure the film thickness, to watch microstructure of the film cross-section and studied the surface morphology. **[15]**

Vazz *et al.* (2004) Express his article work comprises on the preparation of single layered zirconium oxynitride, ZrNxOy, thin films, stored by Rf receptive magnetron sputtering. Atomic force microscopy (AFM) perception shows lower estimations of surface roughness for low oxygen divisions and a second region where roughness develops essentially. At a bias voltage of _75 V, roughening is again watched. The little increment of film hardness in low oxygen divisions ZrNxOy films was credited to grid bends happening because of the conceivable oxygen fuse inside the ZrN cross section and furthermore grain estimate decrease. As to varieties, it was watched a reasonable reliance of the obtained correlation with oxygen division. **[16]**

Rawal *et al.* (2010) Refer his article the present work examines basic, optical and hydrophobic properties of zirconium oxynitride films kept on glass substrates by receptive RF magnetron sputtering. Auxiliary change from Zr_2ON_2 to all around arranged m-ZrO_2 is seen as oxygen partial pressure is increased beyond 4.0% when stored in helium because of penning ionization. The thicknesses of the films were analyzed by surface profilometer and firmly coordinated with the determined one from transmission information. The optical properties of the films were estimated by UV– Vis– NIR spectrophotometer and transmittance of ~99% in the noticeable locale of the range was accomplished. The band gap increments with increment in oxygen halfway weight and is higher in N_2 +He mixed than in N_2 +Ar mixture. **[17]**

Sr. No.	Researchers	Substrate & Film	Coating parameters	Results
1	**Carvalho *et al.*** (2005)	Si (ZrO_XN_Y)	-Time: 60 min Temperature: 400°-800° -Base Pressure: 10^{-4} Pa -Ar gas flow rate: 100sccm	Thickness: 300 nm -2θ = 40°
2	**Cunha *et al.*** (2006)	Stainless Steel (AISI 316) (ZrN_XO_Y)	Temperature: 300 °C -Working pressure: 10^{-4} Pa -RF Power: 800 W -Ar gas flow rate: 100 sccm -Time: 60 min	-2θ = 35° -Thickness: 2.3 ± 0.2 – 9.6 ± 0.4 µm
3	**Huang *et al.*** (2008)	Stainless Steel (AISI 304) (ZrN_XO_Y)	Temperature: 400 – 800 °C -Base Pressure: 8*10^{-4} Pa -Ar gas flow rate: 156 sccm -Oxygen gas flow rate: 8 sccm -Time: 50 min	2θ = 25° - 65° -thickness: 400 – 725 nm -Roughness: 0.8-1.7 nm -Grain size ≤ 14 nm
4	**Huang *et al.*** (2011)	Stainless Steel (AISI 316) (ZrN_XO_Y)	Temperature: 500 °C -Oxygen gas flow rate: 2 sccm -Base pressure: 2.67*10^{-4} Pa -Nitrogen gas flow rate: 5 sccm -Time: 120 min	-Film thickness: 36-69nm -Film hardness: 10 – 22.5 GPa -2θ = 29-36°
5	**Rawal *et al.*** (2011)	Silicon (Zr_2ON_2)	-Nitrogen gas flow rate: 25 sccm -Target distance: 50 mm Temperature: 400 °C Time: 60 min -Pressure: 3.33 Pa	2θ > 90°

Zhu *et al.* (2008) State in his article ZrOxNy thin films have been set up by radio frequency magnetron sputtering at different substrate temperatures. The impact of substrate temperature on auxiliary, optical properties and energy band arrangements of as-kept ZrOxNy thin films are researched. Atomic force microscopy results demonstrate the diminished root-mean-square (RMS) values with substrate temperature. Fourier change infrared spectroscopy spectra demonstrate that an interfacial layer has been shaped between Si substrate and ZrOxNy thin films amid affidavit. X-ray photoelectron spectroscopy and spectroscopy ellipsometry (SE) results show the expanded nitrogen joining in ZrOxNy thin films and in this manner, the decreased optical band gap (Eg) values because of the increased valence-band greatest and brought down conduction band least. **[18]**

Rebouta *et al.* (2004). Studied his article the arrangement of single layered zirconium oxynitride, ZrNxOy, thin films, kept by RF reactive magnetron sputtering. The testimonies were done by changing the procedure parameters, for example, substrate predisposition voltage and flow rate of the reactive gases. Ion bombardment advanced a continuous smoothing of the surface up to a bias voltage of _66 V. At a predisposition voltage of _75 V, roughening is again studied. The little increment of film hardness in low oxygen parts ZrNxOy films was attribute to lattice distribution happening because of the conceivable oxygen corporation inside the ZrN lattice and also grain size decrease. Regarding to colour variation, it was observed a clear dependance of the obtained coloration with oxygen fraction. **[19]**

Cubillios *et al.* (2014). Refer his article ZrOxNy/ZrO2 thin films were kept on tempered steel utilizing two unique strategies: ultrasonic spray pyrolysis-nitriding (SPY-N) and the DC unbalanced magnetron sputtering strategy (UBMS). For UBMS, the film was kept in an air of air/argon with a _air/_Ar stream proportion of 3.0. Basic investigation was helped out through X-ray diffraction (XRD), and morphological examination was done through scanning electron microscopy (SEM) Chemical examination was done utilizing X-ray photoelectron spectroscopy (XPS). Upon synthetic examination of the surface, the coatings showed spectral lines of Zr_3d, O_1s, and N_1s, normal for zirconium oxynitride/zirconia. SEM investigation demonstrated the homogeneity of the films. Zirconium oxynitride films upgraded the tempered steel's protection from erosion utilizing the two methods. The result shows that the layers give great protection from corrosion when the chloride contain is available. **[20]**

Oliveira *et al* (2018). States in her article Metallic Oxynitride are materials of interest, since they represent the combination between the properties of the individual nitrides and oxides. The thermal stability of the oxynitride films is significant for various applications, however it must be separated from oxidation opposition. For this assessment, x-ray diffraction (XRD) patterns have been gained in situ during heated under the two unique atmosphere to maintain a strategic distance from external oxidation (vacuum and a He/H2 mixture). Such tests were performed on chosen Zr-O-N films showing different composition and phases (metal-rich N-insufficient nitride, (oxy)nitride, and O-rich confused oxynitride). The impact of the expansion of Ti has been considered in films including additionally TiN-like stages. **[21]**

Signore *et al.* (2012). State in his article zirconium oxynitride is developing with the consideration for zirconium nitrides stage at high zirconium content. In this work the previously mentioned two stages are acknowledged by RF magnetron sputtering method. The portrayal results, represented in the recent paper, push towards the proof of advancement from zirconium N-rich nitride to the oxynitride films by presenting a little rate (0.5%) of water vapor in a sputtering environment made just of nitrogen gas. Specifically, auxiliary investigation distinguished zirconium N-rich nitride as c-Zr3N4 and zirconium oxynitride as c-Zr2ON2. The development of zirconium oxynitride is because of oxygen nearness, originating from the water separation in the plasma. **[22]**

Chang *et al.*(2007). Refer his article the optimum deposition of ZrN thin film from our previous investigation, by differing oxygen stream rate running from 0 to 8 sccm, monocrystalline ZrNxOy flimsy movies were kept on p-type (100) Si substrates utilizing hollow cathode release ion plating (HCD-IP) system. The oxygen substance of the slight film, decided utilizing X-beam photoelectron spectroscopy (XPS), increased with increasing oxygen flow rate. As the oxygen content increased, the shade of the ZrNxOy thin film changed from brilliant yellow to blue and afterward slate blue, and the microstructure seen by scanning electron microscopy (SEM) shifted from columnar structure to better grains final level and featureless structure. The film properties demonstrated reliable pattern with stage partition. At the point when ZrO2 division was over 30%, the films for the most part displayed the properties of ZrO2. **[23]**

3. Conclusion

From the literature reviews it was observed that zirconium based coatings has band gap values in range 2.0-5eV, optical range from 3 – 3.5eV, their hardness increases up to 40GPa with sufficient modulus of elasticity. Hydrophobicity of zirconium based coating was constituent in the literature revived. The Zr films are typical representatives of carbon-free low electronegativity metal compounds with (i) weak bonds with water, i.e. with a strong hydrophobic effect, and (ii) mechanical properties resulting in their enhanced resistance to cracking.

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