Consequences of N_2 gas flow variation on properties of zirconium oxide-nitride films

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Abstract. Zirconium oxide-nitride films was prepared by RF reactive magnetron sputtering in presence of helium, oxygen and nitrogen gases. The N_2 gas flow rate was varied for each consecutive run of sputtering at values of 66, 72, 78, 84, and 90 sccm respectively. Zirconium oxide-nitride films showed structural variation in evolution of various textures as detected by X-ray diffraction. It showed good transmission values above 50% for all samples. Wettability studies of zirconium oxide-nitride films was done by contact angle goniometer. All samples depict hydrophobic behaviour as all films have contact angle values above 90° and as nitrogen gas flow rate increases, the films roughness as well as contact angle increases. Tribological test is done on zirconium oxide-nitride films coated on aluminium, brass and mild steel pins, which give excellent wear resistance compared to uncoated pins.

KEY WORDS: Zirconium oxide-nitride; Sputtering; Wettability; Hydrophobic; Tribology

1. Introduction

In recent times, thin films are gaining importance because of their decorative, tribological, self-cleaning, and many more properties. Zirconium oxide-nitrides are one of them having excellent properties like anti corrosion [1], high hardness [2], and hydrophobicity [3]. Zirconium oxide-nitride has attracted researchers because it has properties in between zirconium oxides that have high corrosion resistance and zirconium nitrides that have high hardness. Moreover, it can also be deposited by using air as a reactive gas therefore eliminating the mandatory requirement of oxygen and nitrogen gas cylinders [4], [5].

Zirconium oxide-nitride films are synthesized by many methods including ion plating [6], cathodic arc evaporation [7], metal organic chemical vapor deposition [8], and sputtering [1]–[3], [9]–[18]. Sputtering is relatively very old technology and was reported by Wright in 1877. The power source used for creating the plasma while sputtering is either DC or RF. The main disadvantage of DC power is when reactive gases are used, target poisoning occurs which slows the deposition rate and sometimes arcing occurs during sputtering process which leads to damaging substrate as well as power supply. So to avoid this effect, RF power supply is used [19]. It has been observed that usage of helium as an inert gas is not very popular among researchers as only few of them have reported its use [13]. The reason for using helium is that its mass is lower as compared to argon. Therefore, when films are prepared in helium atmosphere, the atoms that are ejected will have to travel short distance in order to get thermalized due to its low atomic mass as reported by Westwood [20].

The purpose of this work is to prepare zirconium oxide-nitrides films using target of zirconium by reactive magnetron sputtering. The inert gas used for generation of plasma is helium and RF power is applied to target material. The effect of nitrogen flow rate variation on structural and wettability properties are inspected. Wear of zirconium oxide-nitride coated and uncoated pins of aluminium, brass and mild steel is measured by pin on disc apparatus by varying rotational speed and load. To test the wear at different parameters, Taguchi design of orthogonal array is done thereby reducing number of experiments compared to full factorial design and the results gained are comparable to full factorial design.

2. Experimental details

Zirconium oxide-nitride films were prepared using custom made sputtering instrument made by Excel instruments, India as shown in figure 1. The sputtering was carried out using zirconium as a target (50.8mm diameter, 5mm thick), two reactive gases: oxygen, nitrogen and helium as inert gas.

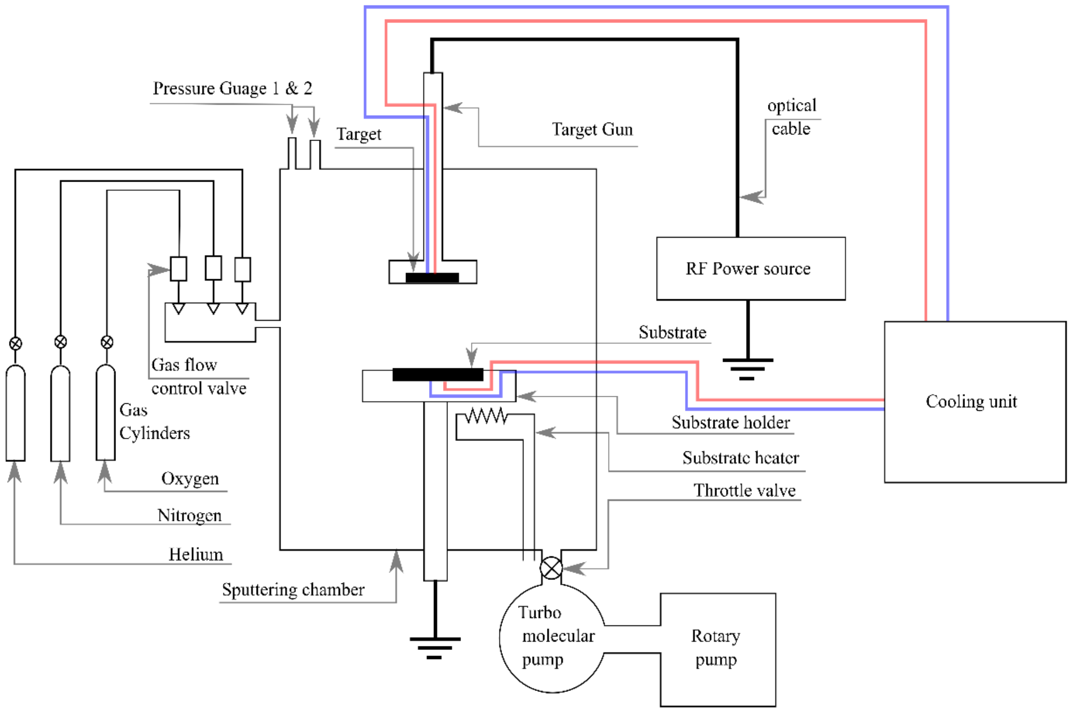

Figure 1. Schematic diagram of sputtering system

All consumable materials used while using sputtering are having 99.99% purity. The base pressure attained before sputtering was 7×10^{-4}Pa and the sputtering was done at 2.50Pa. The target was sputter cleaned for 3 minutes exactly before all the depositions. The helium and oxygen gas flow was kept constant at 10 and 1.5 sccm respectively for all the five runs of sputtering. Nitrogen gas flow was varied at 66, 72, 78, 84, and 90 sccm for different runs and the corresponding sample names are N11, N12, N13, N14, and N15 respectively. The mass flow controller used for transferring the gases from cylinders to the sputtering chamber is made by Alicat scientific, USA. The RF power source used was of Advanced energy, USA and value of power was fixed at 180W. The deposition temperature was kept constant at 500°C and distance between target and substrate was 50mm.

The structural properties of zirconium oxide-nitride thin films were examined with X-ray diffraction method using Bruker D2 phaser X-ray diffractometer with Cu-kα radiation with wavelength 1.54Å. Optical properties were examined by using Shimadzu model 3600 plus (UV-Vis-NIR spectrophotometer). Wettability properties of the films were measured by Rame-Hart model 290 goniometer. Atomic force microscopy is used to find surface roughness and morphology of thin films by using Nanosurf easyscan 2. Scanning electron microscopy (Zeiss Evo 18) was done on the samples to examine the structure of films. There are three sets of coatings and each set consists of one aluminium, one brass, and one mild steel pin. The parameters selected to coat the three sets of pins are minimum, intermediate and maximum nitrogen flow rate variation represented by samples N11, N13, and N15 respectively. These pins are wear tested on pin on disc apparatus made by Ducom industries, USA.

3. Results and discussion

X-ray diffraction graphs of zirconium oxide-nitride thin films prepared at varying nitrogen flow rate is shown in figure 2. The three main peaks observed are (311) and (222) of zirconium oxide-nitride and (111) of zirconium oxide. The deposited zirconium oxide-nitride thin films are having colour variation from golden yellow to blue and blue to violet region for all the samples starting from N11 to N15 which is similar to the results gained by Carvalho et al. 2015 [21]. Oxygen flow rate was kept very less as compared to nitrogen as zirconium is more reactive with the former as compared to later [22].

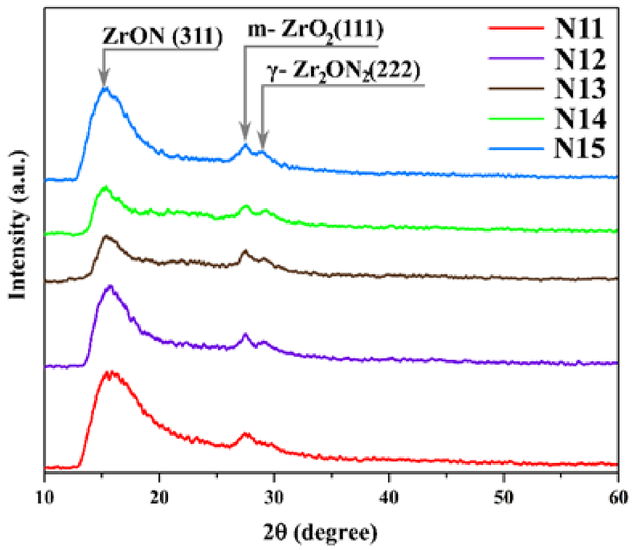

Figure 2. XRD graphs of zirconium oxide-nitride films prepared at different nitrogen flow rate

It is observed that (311) and (222) peaks of zirconium oxide-nitride keeps on increasing with increase of nitrogen gas flow rate. It may be due to the reason that at lesser flow rate of nitrogen, the probability of formation of Zr_2ON_2 is less and as flow rate of nitrogen increases it leads to formation of (311) and (222) textures of zirconium oxide-nitride. In our case, (111) peak of zirconium oxide is also observed due to good chemical affinity of zirconium towards oxygen.

Cubillos et al. 2013 [23] did characterization of zirconium oxide-nitride films prepared by unbalanced magnetron sputtering on AISI 304 and AISI 316 substrates and observed (222) peak of cubic phase Zr_2ON_2. Portinha and Teixeira 2008 [9] deposited reactively magnetron sputtered zirconium oxide-nitride coatings using variation of nitrogen and oxygen both gases and got similar results of X-ray diffraction. Rawal et al. 2014 [3] deposited zirconium oxide-nitride films by varying nitrogen gas flow rate and found out two peaks corresponding to ZrO_2 and Zr_2ON_2. Similarly, other researchers [5], [10], [24] have also found presence of mixed peaks zirconium oxide-nitride and zirconium oxide. So our results are in good agreement with results reported in literatures. The grain size of oxide-nitride films are found by Scharrer formula [25]. The average crystallite size of zirconium oxide-nitride films are around 8-9nm.

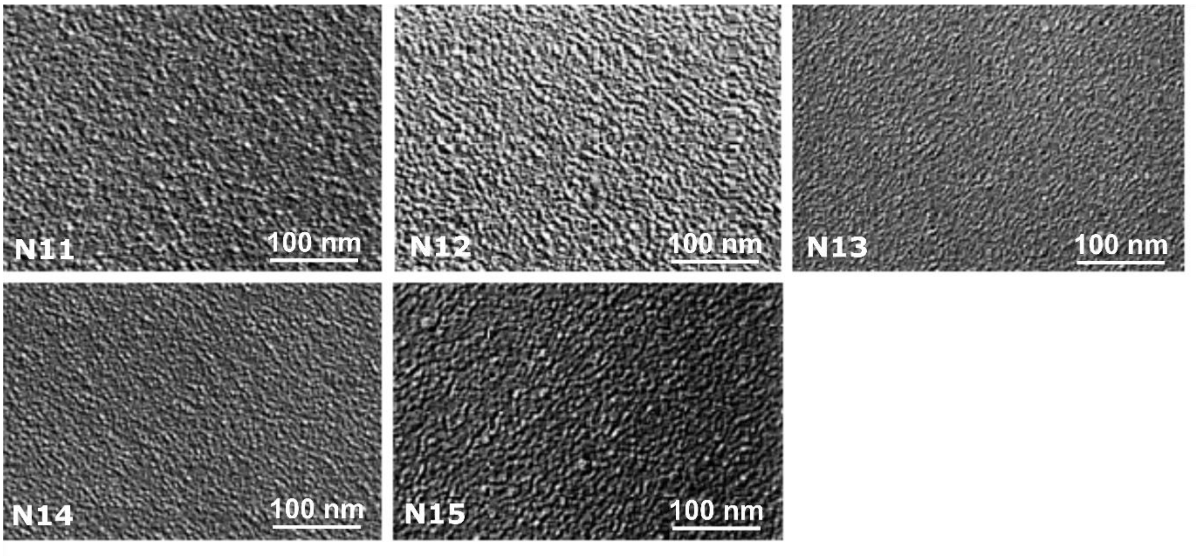

Figure 3. SEM images of zirconium oxide-nitride films prepared at different nitrogen flow rate

SEM images of zirconium oxide-nitride films prepared at different nitrogen flow rate are shown in figure 3. The SEM image shows that there are no voids on the film and so it can be said that there is mixed growth (Stranski- Krastanov model) on the substrate while sputtering [26]. The SEM images show that there is uniform deposition of thin film for all the samples N11, N12, N13, N14, and N15 respectively. The average crystallite size variation of zirconium oxide-nitride films is also negligible having similar values as evident from SEM images thereby confirming XRD results. The AFM images of zirconium oxide-nitride films deposited at varying nitrogen flow rate are shown in figure 4. It is observed that zirconium oxide-nitride films are dense, uniform and having smaller grains hence backing the results of SEM and XRD.

The relation between surface roughness and contact angle of zirconium oxide-nitride films prepared at different nitrogen flow rate is shown in figure 5. Surface roughness and contact angle share a direct relationship. The increment of both surface roughness and contact angle are identical with the rise in flow rate of nitrogen as observed from figure 5. This states that a direct relationship between surface roughness and contact angle is established for zirconium oxide-nitride films.

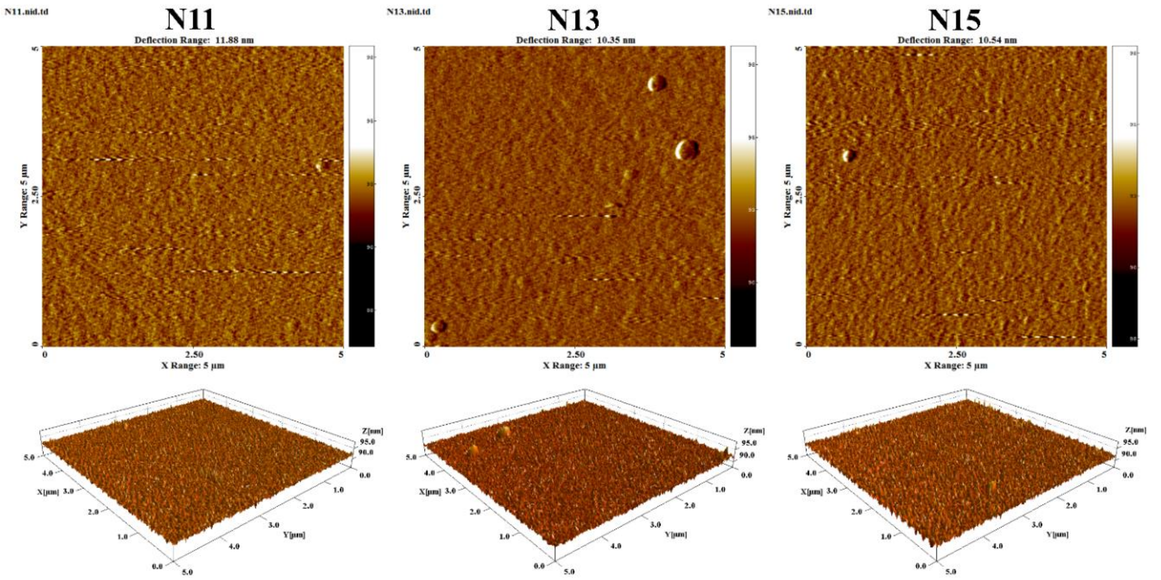

Figure 4. AFM micrographs of zirconium oxide-nitride films prepared at different nitrogen flow rate

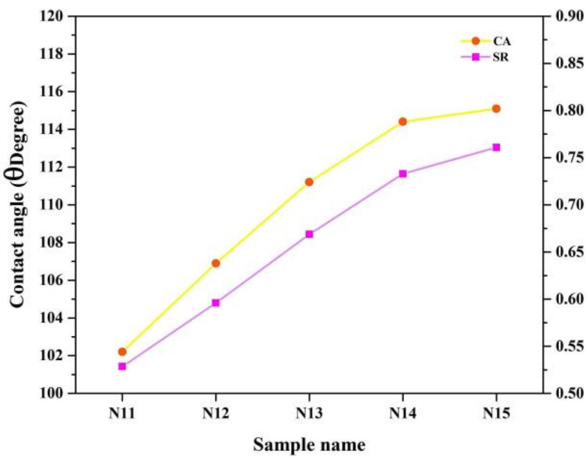

Figure 5. Surface roughness and contact angle of zirconium oxide-nitride films prepared at different nitrogen flow rate

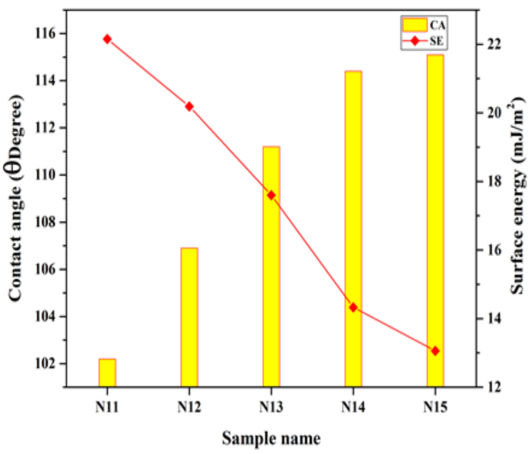

Figure 6. Surface energy and contact angle of zirconium oxide-nitride films prepared at different nitrogen flow rate

Surface energy of deposited zirconium oxide-nitride films was found by Wu method. Surface energy and contact angle of zirconium oxide-nitride films prepared at varying nitrogen flow rate is shown in figure 6. The surface energy and contact angle of fluid share an inverse relationship. Rawal et al. 2014 had observed that as the roughness of film increases, hydrophobicity also increases [3]. In our case, increase in nitrogen flow rate leads to increase of contact angle values. So as the contact angle values of zirconium oxide-nitride films increases a decline in their surface energy values is observed as evident from figure 6.

The transmittance spectra of zirconium oxide-nitride films deposited at varying nitrogen flow rate is shown in figure 7. It is observed that increase in nitrogen flow rate leads to decline of transmission values for zirconium oxide-nitride films.

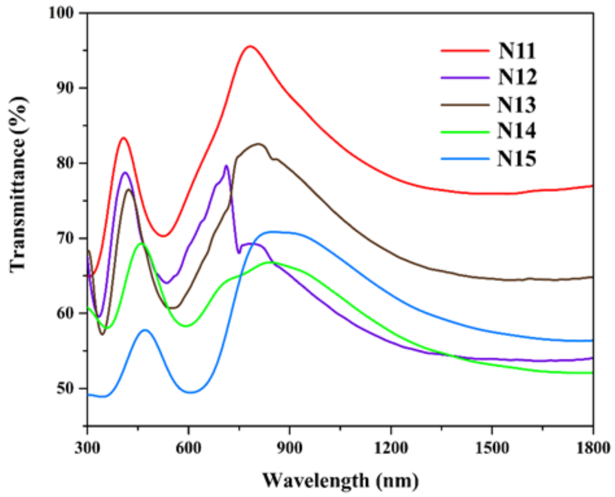

Figure 7. Transmittance spectra of zirconium oxide-nitride films prepared at different nitrogen flow rate

To test the pins on pin on disc apparatus, the parameters have to be decided including speed and load. Here, first of all the experiments with uncoated pins are carried out and in which they are tested for various parameters until the best parameters for wear test are available. So after doing various experiments on uncoated pins, the data which have been decided for doing wear test for coated pins are shown in table 1.

Table 1. Parameters and their levels for wear measurement of zirconium oxide-nitride films

Factor	Units	Level 1	Level 2	Level 3
Speed	rpm	275	550	825
Load	N	4.5	6.5	8.5
Material	-	Al	Brass	MS

Taguchi design has two approaches; one is full factorial design and other one is orthogonal array. In full factorial design, 27 experiments have to be carried out and in orthogonal array, 9 experiments have to be carried out. In Taguchi method, the desirable value for the output characteristics is termed as signal or mean and the undesirable value is termed as noise or standard deviation. Signal to Noise proportion is utilized to measure the quality characteristic changing from the desired value. The parameters and their levels for wear measurement is given in table 1. The corresponding L9 orthogonal array for wear measurement is given in table 2.

Table 2. L9 orthogonal array for Taguchi design of zirconium oxide-nitride films

Exp. No.	Machining parameters			Response
	Speed (rpm)	Load (N)	Material	Wear (µm)
1	275	4.5	Aluminium	68.12
2	275	6.5	Brass	70.84
3	275	8.5	MS	55.96
4	550	4.5	Brass	72.19
5	550	6.5	MS	60.65
6	550	8.5	Aluminium	98.54
7	825	4.5	MS	61.18
8	825	6.5	Aluminium	100.19
9	825	8.5	Brass	89.32

The coated pins are wear tested (machined) on pin-on-disc apparatus. Pins were subjected to wear with the rubbing action between pins and rotating disc. The pins are subjected to loading condition so wear can be measured under load. So, in machining parameters, speed of disc, load on pins and material of pins are changed. Here, all the pins are of 10mm diameter. The pin-on-disc apparatus measures the wear of pins by measuring height of pin before and after machining. So, wear of the pins is in the form of height reduction that is measured in micron.

We have first decided all the parameters in Taguchi design and then by using those parameters, all responses related to wear of different pin materials is found. The responses are found using pin on disc apparatus by using parameters given in table 2. The influence of various parameters on wear of pins is obtained. Table 3 represents response table for signal to noise ratios of zirconium oxide-nitride films. The findings that can be drawn from table 3 is that parameters effecting most the wear of pin is material ranked as 1st, speed that is ranked 2nd and load that is ranked 3rd. This indicates the most influencing parameter in wear test for pin. These parameters are applied to coated pins and wear rates are found out based on this approach.

Table 3. Response table for Signal/Noise Ratios (Smaller is better) of zirconium oxide-nitride films

Level	Speed (rpm)	Load (N)	Material
1	-36.21	-36.52	-38.85
2	-37.57	-37.56	-37.73
3	-38.26	-37.95	-35.45
Delta	2.05	1.43	3.40
Rank	2nd	3rd	1st

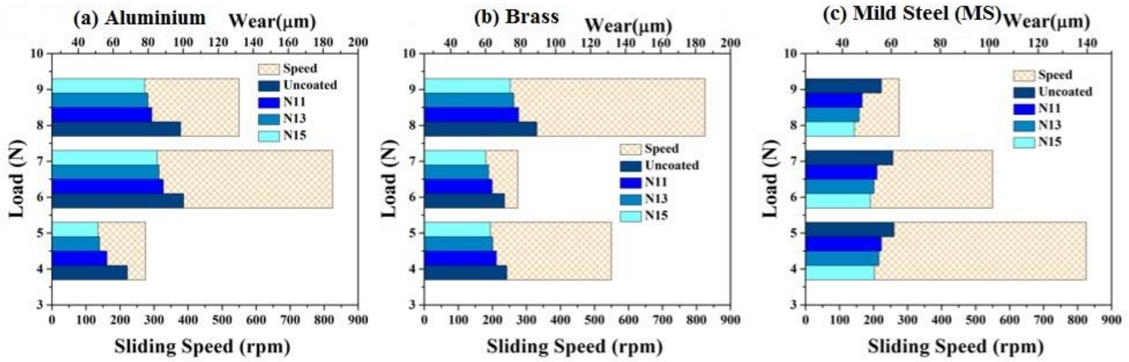

Figure 8. Wear of zirconium oxide-nitride films prepared at different varying nitrogen flow rate on pins of (a) aluminium (b) brass (c) mild steel (MS)

Wear of zirconium oxide-nitride films deposited at varying nitrogen flow rate on pins of aluminium, brass and mild steel (MS) for uncoated and coated pins as per samples N11, N13 and N15 are shown in figure 8. It is observed that wear is lesser for coated aluminium, brass and mild steel (MS) pins and more for their respective uncoated pins. However, it also depends upon the type of material on which the coating is done. The harder the material is the more wear resistance it gets when coated with zirconium oxide-nitride films. Zirconium oxide-nitride films improves wear resistance for all materials including brass, mild steel and aluminium. The trend followed by coated aluminium, brass and mild steel (MS) pins for wear tests is that as the nitrogen gas flow rate increases, wear rate decreases. The reason may be it might have led to hardness increment in zirconium oxide-nitride films.

4. Conclusion

Zirconium oxide-nitride thin films depicts (311) peak as nitrogen flow rate increases from 66 to 90 sccm. The roughness of zirconium oxide-nitride film increases from 0.5285 to 0.7609nm and contact angle increases from 102.2° to 115.1° with the increment in nitrogen gas flow. The most influencing parameter for wear rate is material of pins. The wear resistance of zirconium oxide-nitride films improves with increase of nitrogen flow rate. It is observed that for minimum wear, nitrogen flow rate while sputtering should be higher, so pins coated at 90 sccm nitrogen flow are more wear resistant than others.

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