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COMMUNICATIONS

# The influence of substrate bias voltage on the electrochemical properties of ZrN thin films deposited by radio-frequency magnetron sputtering: Biomedical application

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In order to study the influence of the substrate bias on the properties of ZrN thin films deposited by radio-frequency magnetron sputtering for biomedical application. Films of ZrN were grown onto 316L stainless steel substrate using radio-frequency (rf) magnetron sputtering from a pure zirconium target in Ar - $N_2$ gas mixture. The substrate bias voltage was varied from 0 to −100 V, which produces a variation in the structural and electrochemical properties of the obtained films. The deposited films were characterized by X-Rays Diffraction, Atomic Force Microscopy, scanning force microscopy and potentiodynamic polarization.

Keywords: ZrN, 316L stainless steel, RF magnetron sputtering, bias voltage, corrosion

## 1 Introduction

Zirconium nitride has been recognized as a leading material of high hardness, exceptional thermal and chemical stability with low electrical resistivity [1, 2]. Thus, it has been widely used as a protective and decorative coating [3, 4] and as a diffusion barrier in the microelectronics industry [5-8]. In general, there are many methods to synthesize a zirconium nitride film such as the ion beam assisted method [9], the cathodic arc evaporation method [10], the sputtering method [11], etc. Among these methods, reactive magnetron sputtering is a very important method because the stoichiometry of the deposited film and a metal target can be used. Moreover, it is one of the simplest and widely used methods in the industry. In the literature, the effect of the reactive sputtering gas mixture between cathodic sputtering and reactive magnetron sputtering on several zirconium nitride film structures has been studied [13, 14]. The behavior of ZrN films in a bacteriological environment were also realized [15]. Parameters like surface roughness and chemical composition of the implant surface were found to have a significant impact on plaque formation. In this paper, Zr-N coatings were deposited on 316L stainless steel using radio frequency magnetron sputtering with various bias voltages to investigate its structural, surface and electrochemical properties.

## 2 Experimental details

Zirconium nitride films were deposited on 316L stainless steel using RF-magnetron sputtering. Metallic zirconium with a purity of 99.99 % and a diameter of 3 inches was used as a sputtering target. Ar (purity of 99.9999 %) and $N_2$ (purity of 99.9999 %) were used as sputtering gas and reagents, respectively. A negative bias voltage of 0, 50 and 100 V was applied to the substrate. In order to increase the ionization degree of the Zr target by the ion bombardment enhancementa negative bias was applied to the substrate.In fact, the appropriate optimization of the ion bombardment by negatively biased substrate ($\leq$I100IV) may to avoid the damage of the growing film and the creation of a large number of defects in the films. During heavy ion bombardment, densification of the microstructure also occurs through the enhanced surface mobility of adatoms, which eliminates film porosity. It also increases the strain energy in the film, thereby influencing the formation of textured grains during film growth [16].

The gas ratio of $N_2$ in gas mixture ($Ar + N_2$) and the deposition time were kept constant at 0.16 and 60 minutes, respectively. The coating conditions of samples were given in Tab. 1. The crystalline structure of the films was characterized by an X-ray diffraction technique with Cu-Ka radiation ($\lambda$ = 1.54056 Å). The average crystallite size of the ZrN films was calculated according to Scherrer's formula

$$L = \frac{0.89\lambda}{\beta \cos\theta}.$$

where $\lambda$ is wave length of x-ray, $\beta$ is full width at half maximum and $\theta$ is the diffraction angle.

The thickness and morphology of the films were analyzed using scanning electron microscopy. Measurements

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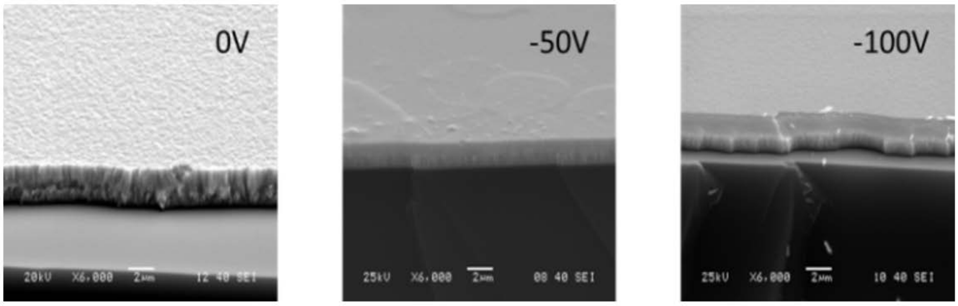

**Fig. 1.** The SEM images of ZrN thin films coated with 0 V, −50 V and −100 V bias voltages

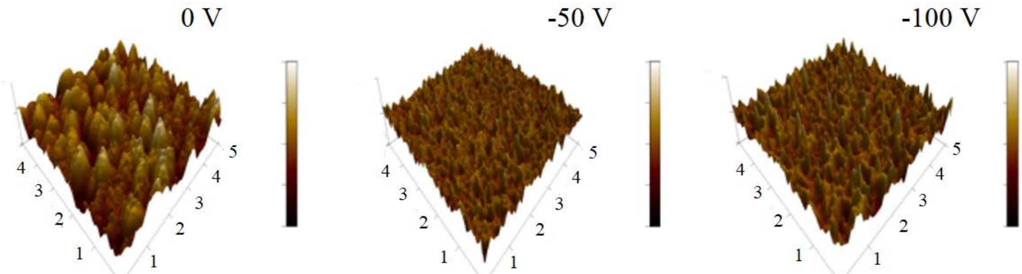

**Fig. 2.** 3D AFM images of ZrN thin films with bias voltage 0 V, −50 V and −100 V

**Table 1.** Coating conditions of samples

| Target | Pure zirconium 99.99 % |
|---|---|
| Target-Substrate distance | 30 mm |
| Sputtering gas | Argon |
| Reactive gas | Nitrogen |
| Reactive composition gas ($N_2/Ar+N_2$) % | 16 |
| Working gas pressure | 20 mTorr |
| Sputtering power | 250 W |
| Bias substrate | 0, −50, −100 V |
| Time deposition | 60 min |
| Substrate temperature | Not heating |

of the surface roughness were obtained from topographic images from an Atomic Force Microscope (MFP-3D from Asylum Research an Oxford Instruments company).

The characterization of the mechanical properties of the deposited layers was carried out by a CSM Instrument Switzerland nanoindenter equipped with a Berkovich diamond indenter. The device is controlled by a computer system whose software makes it possible to directly obtain the values of hardness and Young's modulus. The charge to be applied to the indenter has been optimized so as to remain within the range of validity of the hardness measurement, that is to say not exceeding 10 % of film thickness for the depth of indentation. A load of 5 mN is applied in 30 seconds.

The electrochemical tests carried out on the coated and uncoated 316L steel were carried out using a galvanostatpotentiostat of the PARSTAT 400 type. The solution used in this study is a simulated solution of a physiological medium, namely the Hank's solution.

## 3 Results and discussions

Figure 1 shows the typical SEM images of ZrN grown in pure Ar and $N_2$ mixture with various bias voltages. All the depositedfilms we report here show similar topography, the microstructure had the columnar grains with the growth direction perpendicular to the surface of substrates and the grain sizes in the range of a few nanometers, Tab. 2. It can be seen also that the surface becomes smoother as the bias was applied to the substrate compared to the unbiased surface, indicated by SEM, Fig. 1 and AFM images Fig. 2.

The surface roughness of the ZrN surface films was attained by an analytic software Nanoscope and summarized in Tab. 2. The higher roughness 10.2 nm is obtained for the unbiased surface film and it decreases to the lowest 2.2 nm at −50 V. The surface roughness then increases to 2.8 nm at −100 V.

Further results are shown in the SEM images results where the thickness can be obtained and the deposition rate calculated. Cross-sectional SEM of a sample shown in Fig. 1 shows a uniform substrate surface. Moreover, it provides the thickness of the deposited films. The highest thickness value outcome is 2000 nm. The deposition rate can be calculated by dividing the crosssectional thickness by the deposition time. Hence, the maximum deposition rate is 33.3 nm/minute obtained for the unbiased sample.

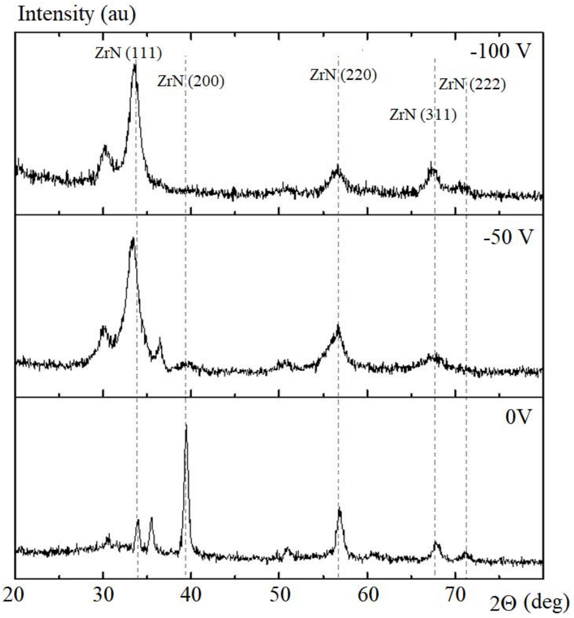

**Fig. 3.** XRD pattern for ZrN thin film with different bias voltage

**Table 2.** Thicknesses, deposition rate, grainssize, roughness, $H/E$ and $H^3E^2$ ratios of ZrN films at different bias voltages

| Samples | S1 | S2 | S3 |
|---|---|---|---|
| Substrate bias (V) | 0 | −50 | −100 |
| Roughness rms (nm) | 10.2 | 2.2 | 2.8 |
| Grain size $L$ (nm) | 17 | 6 | 5 |
| Thickness (nm) | 2000 | 1430 | 1610 |
| Deposition rate (nm/min) | 33.3 | 23.8 | 26.8 |
| $H/E$ | 0.095 | 0.123 | 0.130 |
| $H^3/E^2$ (GPa) | 0.240 | 0.562 | 0.669 |

The Zirconiumnitrogen system contains refractorynitrides. But the stability and microstructures of these zirconium nitrides phases are still not completely understood. According to the phase diagram provided by Gribaudo *et al* [17, 18], ZrN is crystalline face centred cubic (fcc), rock salt structure (space group Fm3m), whereby the nitrogen atoms occupy the interstitial octahedral sites. The rocksalt ZrN was found to have the lowest enthalpy of formation. Besides ZrN, substoichiometric $Zr_2N$ (space group $P4_2$/mnm), $Zr_4N_3$ (space group C2/m), $Zr_6N_5$ (space group C2/m) and $Zr_8N_7$ (space group C2/m) can be thermodynamically stable at ambient conditions.

The results of X-ray diffraction (XRD) analysis performed on the ZrN films deposited under different negative substrate bias voltages are shown in Fig. 3. The patterns show that the deposited films are crystalline and consisted of pure ZrN face centred cubic for both conditions unbiased and biased. For the film deposited at an unbiased voltage, the highest (200) diffraction peak intensity indicate that (200) is preferential orientation. Its show also other peaks with lower intensities (111) (220) (311) and (222). While for the biased conditions, the films grown at −50 V and −100 V showed almost complete disappearance of peak (200) and high intensity peak (111) which is the preferred orientation. Niu *et al* [19] also reported a similar variation trend of cathodic arc films at a variation bias voltage. It is also observed that the peaks are wider compared to those of films deposited with unbiased voltage.

Both nanohardness and elastic Young modulus values of ZrN films were calculated from the nanoindentation loading and unloading curves using nanoindenter (CSM) system with Berkovich-diamond indenter software and plotted in Fig. 4. The nanohardness values for ZrN samples increases from 26.3 to 39.3 GPa as the substrate bias increase. Notice that the average of ten measurements, and the measurement depth corresponding to approximately 10 % of the thickness of the films. In addition, from Fig. 4, we can see that the minimum hardness, obtained for unbiased conditions, is 6 times higher than 4 GPa hardness of the substrate.

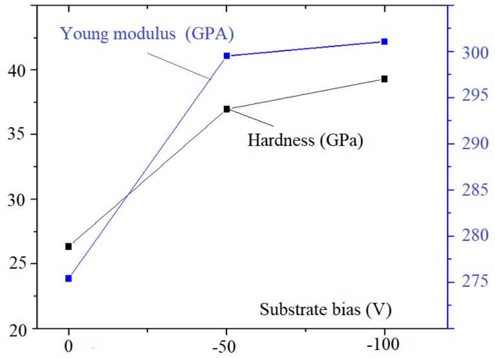

**Fig. 4.** The dependence of nanohardness and Young's modulus on the substrate bias

The variation of hardness and Youngs modulus can be attributed to the variation of structure with substrate bias. It is known that several factors could affect the film hardness, such as the preferred orientation and grain size. In addition, the mechanical property of ZrN is strongly related to its preferred orientation, the biased films with (111) preferred orientation possesses the highest hardness. The same results have been reported for other nitrides like TiN [20]. Niu *et al* [19] have also reported with increasing substrate bias leads to the densification and the decrease defect density, which correspond to the increase of hardness and Young's modulus. Beside the preferred orientation, the grain size could affect the hardness. From the study of grain sizes of ZrN films, the hardness of the films is increase with decreasing grain sizes, which agrees with the Hall-Petch relation. Thus, the increased hardness of ZrN with applied the negative bias to the substrate in the present work can be directly related to the small crystallite size and the (111) orientation.

In other hand, it exist other useful empirical parameters for mechanical characterization of protective films, such as the $H/E$ and $H^3/E^2$ ratios, which are measures

**Table 3.** Electrochemical parameters of potentiodynamic polarization tests obtained from the Tafel method for stainless steel with and without thin film of ZrN (in the operating conditions of the substrate bias) in Hank's Solution

| Samples | Uncoated Steel | S1 | S2 | S3 |
|---|---|---|---|---|
| Substrat bias (V) | – | 0 | −50 | −100 |
| Corrosion Rate, $Cr$ (mpy) | 0.0244 | 0.0451 | 0.0244 | 0.0026 |
| $R_\mathrm{p}$ (M$\Omega$) | 0.402 | 0.160 | 0.149 | 12.155 |
| $E_\mathrm{corr}$ (mV) | −573.171 | −503.828 | −248.5 | −565.166 |
| $i_\mathrm{corr}$ (nA) | 53.7 | 70.1 | 37.9 | 4.12 |
| $P_\mathrm{e}$ ( %) | – | −30 | 29 | 92 |
| $P$ ( %) | – | 76.5 | 1.0 | 2.9 |

of the toughness and resilience of the films, respectively [21, 22]. Toughness can be defined as the ability of a material to absorb energy during deformation up to fracture. Similar to the variation of hardness, the $H/E$ and $H^3/E^2$ ratios increased from 0.095 and 0.24 GPa to the highest values 0.13 and 0.669 GPa, respectively, Tab. 2, with bias from 0 to −100 V, indicating that the negative bias efficiently enhanced the wear resistance and the overall mechanical performance of the films. The $H/E$ ratio was used to determine the limit of elastic behavior of ceramic films and a high $H/E$ ratio was associated with the increased elasticity. High $H^3/E^2$ ratio indicates a high resistance of films to plastic deformation and thus, a high wear resistance, besides low rigidity. Calculated value $H^3/E^2 = 0.66$ GPa indicate improved wear resistance of the films.

Finally, the electrochemical behavior of the ZrN films deposited on 316L steel was studied in a physiological medium (Hank's Solution) at a temperature of 38 °C.

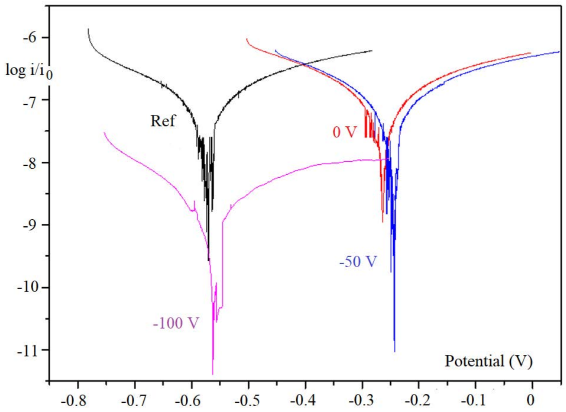

**Fig. 5.** Comparison of potentiodynamic polarization curves for different films

Figure 5 presents the result of cyclic polarization potential of the uncoated and coated substrate steel 316L. The potentiodynamic polarization curves are shifted towards the most anodic potentials may be subjected to the susceptibility to corrosion happen on the surface samples in Hank solution. We notice that the corrosion current decreased with increasing the bias voltage; this may be due to the packing density (as shown in MEB) of the film [23]. The lowest corrosion current is obtained at a bias voltage of −100 V.

The electrochemical parameters were obtained by extrapolation of Tafel lines. The potential corrosion $E_\mathrm{corr}$ and current density $i_\mathrm{corr}$ represent the intersection of the cathode-slope and the anode-slope and corrosion rate $Cr$ of the specimens extracted from the curves. The different results obtained are summarized in Tab. 3. The corrosion current density, $i_\mathrm{corr}$ (nA/cm$^2$), is related to the corrosion rate, $Cr$ (mpy) with using the following equation [24]:

$$Cr = 0.13 \times i_\mathrm{corr} \times \frac{EW}{\rho},$$

where $i_\mathrm{corr}$ in $\mu$A/cm$^2$, $\rho$ and $EW$ is the density and the equivalent weight, respectively. According to this equation, ZrN film deposited at −100 V presented the lower corrosion rate (0.0026 mpy) compared to the uncoated alloys (0.0244 mpy).

It's known that the structure of hard films (TiN, TiC , ZrN … ) presents characteristic defects such as pinholes, microcracks and macroparticles which are generated during the deposition by PVD method [25]. In fact, the defects on the PVD films consist of preferential paths to the diffusion of aggressive species into the substrate under the protective films and it could express these defects by estimate the porosity electrochemically. This porosity was calculated from $E_\mathrm{corr}$ and $R_\mathrm{p}$ measurement deduced from the potentiodynamic polarization technique using the following formula:

$$P = \frac{R_\mathrm{ps}}{R_\mathrm{p}} \times 10^{-|\Delta E_\mathrm{corr}|/b_\mathrm{a}}$$

where $P$ is the porosity of the ZrN film, $R_\mathrm{ps}$ is the polarization resistance of the substrate, $R_\mathrm{p}$ is the polarization resistance of the substrate coated with the ZrN film, $\Delta E_\mathrm{corr}$ is the difference in free corrosion potential between the coated and the uncoated substrate and $b_\mathrm{a}$ is the anodic Tafel slope of the substrate.

Additionally, the film's protective efficiency ($P_\mathrm{e}$) was calculated from the polarization curve using the following equation:

$$P_\mathrm{e} = \left[1 - \left(\frac{i_\mathrm{corr,film}}{i_\mathrm{corr,substrate}}\right)\right] \times 100,$$

where $i_{\text{corr,film}}$ and $i_{\text{corr,substrate}}$ are the corrosion current densities of the coating and substrate, respectively [26]. The results show that all the films, deposited at biased conditions, work as corrosion protective films on stainless steel. And film deposited at $-100$ V gives protection efficiency 92 %. This result could be related to the grain size, Tab. 2, the film exhibiting the lowest grain size gives a high protective efficiency and also good hardness. These results show that the obtained films for the highest substrate bias voltage ($-100$ V) are more protective than the uncoated steel, because the corrosion of metallic biomaterials implants due to the corrosive body fluid is unavoidable, the corrosion resistance is a very important feature in the choice of metallic biomaterials. The implants may release unwanted non-biocompatible metal ions which can shorten its life.

## 4 Conclusion

In this paper, we describe the effect of the substrate bias voltage on the properties of ZrN deposited on stainless steel using RF magnetron sputtering system. It was evident that ZrN films deposited at different negative bias voltages consisted of cfc structure.

The study shown that negative bias voltage has a great effect on the mechanical and electrochemical nature of all the films. The ZrN film deposited at $-100$ V shown the hardest and lowest corrosion rate.

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