



Nitrogen effect on corrosion resistance of ion beam sputtered nanocrystalline zirconium nitride films

M.M. Larijani ^{a,*}, M. Elmi ^b, M. Yari ^c, M. Ghoranneviss ^d, P. Balashabadi ^a, A. Shokouhy ^d

^a Agriculture Medical and Industrial Research School, NSTRI, P.O. Box 31485-498, Karaj, Iran

^b Department of Physics, Karaj Branch, Islamic Azad University, Karaj, Iran

^c Corrosion Lab., Materials Eng. Dep., Islamic Azad University, Tehran, Iran

^d Plasma Physics Research Centre, Islamic Azad University, P.O. Box 14665-678, Tehran, Iran

ARTICLE INFO

Available online 5 March 2009

Keywords:

ZrN
Corrosion
Thickness
Potentiodynamic
XRD

ABSTRACT

This research has studied the effect of $N_2/(N_2 + Ar)$ flow rate ratio ($F(N_2)$) on the microstructure and anticorrosive property of zirconium nitride (ZrN) films deposited on AISI stainless steel (SS) 304 substrates. ZrN films were deposited using ion beam sputtering technique and their corrosion resistance has been investigated via electrochemical test using 0.5 M H_2SO_4 solution. The thickness of the films decreased with increase of N_2 flow rate. Results of X-ray diffraction (XRD) showed that all the films had a preferred crystalline orientation which changed from [220] axis at low $F(N_2)$ to [111] axis at high $F(N_2)$. The electrochemical test revealed that the corrosion resistance increased with increasing (111) preferred orientation. Furthermore, micrographs obtained by scanning electron microscopy (SEM) indicated that damages on the sample surface due to corrosive agent attacks may reduce with increasing film thickness.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

ZrN films have various interesting applications including hard wear-resistant coatings on cutting tools [1,2], diffusion barriers in integrated circuits [3], corrosion resistance on metals in corrosive environment [4,5] and warm golden color in jewelry industry [6].

Hardness, wear and corrosion resistance as well as thermal and electrical properties of ZrN films depend on both deposition technique and processing parameters. In our previous works [7], using ion beam sputtering deposition technique (IBSD) we found that the nitrogen flow rate greatly affects the microstructure and hardness of the films due to the variation of (111) preferred orientation intensity. It is well known that the films deposited using PVD techniques, present numerous defects on their surface such as porosity which in turn, deteriorate the corrosive protection of the films. In this work, we continue to investigate the effect of nitrogen flow rate on the corrosive behavior of IBSD ZrN films.

2. Experimental procedures

ZrN films were prepared by ion beam sputtering on AISI 304 stainless steel substrates using a pure zirconium target and a mixture

of Ar and N_2 gas in the Kaufman ion source with 2.2 keV accelerating energy. The substrates analyzed by X-ray fluorescence spectroscopy (XRF), had a composition of 0.15% C, 0.17% V, 0.72% Si, 2% Mn, 8.98% Ni, 18.81% Cr and the balance being Fe. The substrates ($21 \times 21 \times 2 \text{ mm}^3$) were abraded with 1000, 1200, and 2000 grit silicon carbide papers and were finally mirror polished with $0.03 \mu\text{m}$ aluminum oxide. Prior to deposition, the specimens were ultrasonically cleaned in both acetone and alcohol bath for 5 min and dried with argon gas. After cleaning, the substrates were immediately inserted into the vacuum chamber and fixed on a resistance heater. The coating chamber was evacuated to a base pressure of 1.2×10^{-3} Pa. Meanwhile, the substrates were gradually heated to $400 \text{ }^\circ\text{C}$.

The sputtering was initiated by introducing pure Ar (%99.999) and N_2 (%99.999) gas into the chamber. The working pressure was kept constant at 2.5×10^{-3} Pa and the total flow rate of (Ar + N_2) mixed gas was maintained at 60 sccm. The selection of the deposition conditions was based on the earlier research [7] where the microstructure and properties of ZrN on AISI 304 SS substrate were investigated with respect to substrate temperature. The deposition period for ZrN was 4 h in each run.

The film thickness was measured by a quartz-crystal thickness monitor. The crystal structure and preferred orientation as well as the microstructure of the ZrN films were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. Investigation of the electrochemical corrosion behavior was performed by a potentiostat (EG&G model 273) coupled to PC, potentiodynamic method in a 0.5 M H_2SO_4 solution. The auxiliary and reference electrodes were platinum rod and saturated calomel

* Corresponding author. Fax: +98 261 4411106.

E-mail address: mmojtahedzadeh@nrcam.org (M.M. Larijani).

Table 1
Film thickness as a function of the $F(N_2)$ at 400 °C substrate temperature.

$F(N_2)$ (%)	10	30	50	65	80
Thickness (μm)	3.75	3.70	3.21	2.45	1.92

(SCE) electrode, respectively. The working electrodes were sealed with acrylic resin and left an area of 1 cm² exposed to the solution during test, were also polarized from –250 mV vs. open circuit potential at a scan rate of 0.1 mV s⁻¹. The ends of scanning were selected after considering transpassive behavior in polarization curves. After each experiment the corrosion current (I_{corr}) and the corrosion potential (E_{corr}) were determined using soft corr III software. This software used the slopes of cathodic and anodic branch for extracting the corrosion current. The critical passive current density (I_{crit}) was obtained from the polarization curve. All the presented potentials are as a function of SCE.

3. Results and discussions

Table 1 presents the thickness values of ZrN films deposited on the SS substrates at 400 °C with different $F(N_2)$ defined as: $F(N_2)$ (%) = $N_2(\text{sccm}) / \text{Ar} + N_2(\text{sccm})$.

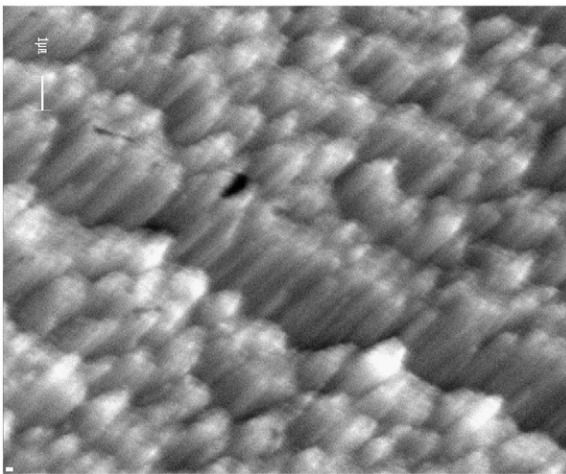


Fig. 1. A typical SEM micrograph for a ZrN film grown at 400 °C with $F(N_2) = 50\%$. The scale is 1 μm .

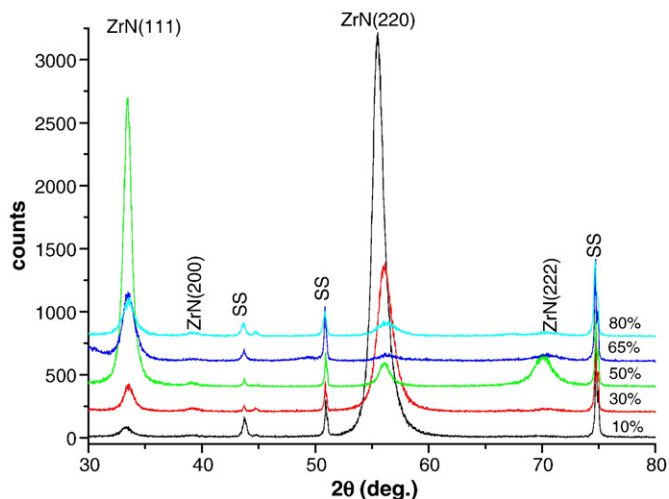


Fig. 2. X-ray diffraction patterns for ZrN thin films on SS 304 with different $F(N_2)$ at 400 °C.

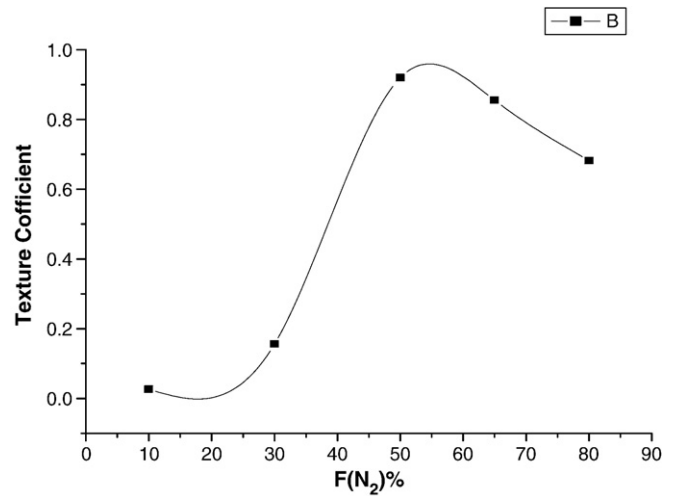


Fig. 3. The variation of (111) texture coefficient with $F(N_2)$.

Decrease of the film thickness with increasing N_2 flow rate, at the same deposition period can be due to i) lower sputtering yield of nitrogen upon replacing argon, leading to a decrease of zirconium sputtered atoms ii) poisoned or nitrided target surface, slower deposition rates because of the low sputter yield of ZrN and iii) resputtering of deposited films by backscattered energetic nitrogen particles reducing the growth rate. Fig. 1 illustrates SEM micrograph of a film titled 30° and prepared at $F(N_2) = 50\%$. It clearly shows a dense columnar structure of ZrN film developed at substrate temperature of 400 °C. We believe that the reason of having such structure at low temperature (T_m is 2980 °C for ZrN) is due to adatom surface mobilities accelerated in our experiments by the bombardment of the growing film with energetic ions which impact the surface tangentially during ion sputtering and backscattered argon and nitrogen neutrals. Both of these phenomena may provide required energy to the adatoms in surface diffusion mechanism instead of increasing the substrate temperature. In accordance to the SEM micrographs, uniformity of the films decreases at high nitrogen flow rates (65% and 80%) with appearing some spots on the film surface. This observation is similar to that of our previous work reported elsewhere [7].

Fig. 2 shows XRD diffraction patterns of all the ZrN coated samples with 2θ scanning from 30° to 80°. According to this figure single phase

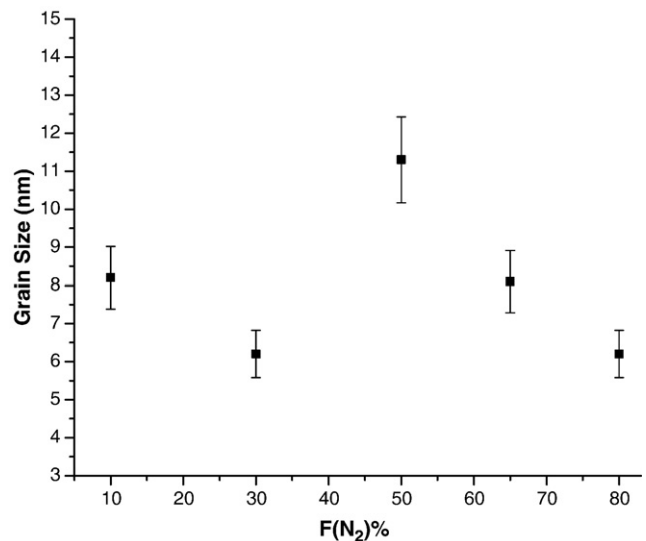


Fig. 4. Grain size of ZrN films versus $F(N_2)$.

Download English Version:

<https://daneshyari.com/en/article/1660184>

Download Persian Version:

<https://daneshyari.com/article/1660184>

[Daneshyari.com](https://daneshyari.com)