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Structural and mechanical properties of ZrN films prepared by ion beam sputtering with varying N_2/Ar ratio and substrate temperature

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Abstract

Zirconium nitride (ZrN) films were deposited by ion beam sputtering technique on stainless steel 304 substrates using a mix of ($Ar+N_2$) gas. In this paper, the effects of $N_2/(N_2+Ar)$ flow ratio ($F(N_2)$) and substrate temperature on the microstructure and microscopic properties of the deposited films were investigated. The phase and the morphology were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) respectively; moreover, the composition depth profile of ZrN was obtained using secondary ion mass spectroscopy (SIMS). In a wide range of $F(N_2)$ (10–54%), the intensity of (1 1 1) peak increased which was the preferred orientation, while for $F(N_2)$ more than 54% the ZrN peak intensity was decreased and the amorphous structure was formed at 95%. The XRD patterns presented a texture change due to the processing temperature, which was varied within the range 200–550 °C. At 400 °C, the (1 1 1) crystalline plane intensity was higher than the other ones, leading to the presence of a preference for this orientation. Good planarity of the deposited films was confirmed by SEM, it did not reveal any undulations, fractures, or cracking. The Vickers micro-hardness tester with a load of 25 g was used to measure the hardness of the films. The results showed that the structural and mechanical properties were strongly influenced by nitrogen ratio and substrate temperature.

Keywords: ZrN; Ion beam sputtering; Stoichiometry; Hardness

1. Introduction

The field of application of hard coating-metal substrates systems has grown up extensively in the past few years [1]. Among the hard coating materials, the transition metal nitride coatings such as TiN have been developed in current decades. Recently, zirconium nitride (ZrN) films have attracted increasing interest for various applications such as diffusion barriers, cryogenic thermometers, decorative coatings and hard coatings because of their better corrosion resistance, lower resistivity, higher mechanical properties and exhibiting warmer golden color than the corresponding properties of TiN [2,3]. However, zirconium has a higher melting point, a lower vapor pressure and higher susceptibility to contamination by oxygen and carbon; thus it is more difficult to deposit ZrN film than TiN or CrN [4,5].

Physical vapor deposition (PVD) methods such as rf sputtering [6], arc-evaporation CVD [3], ion beam-assisted deposition [7] have been widely applied to deposit transition metal nitride films. The properties of ZrN films depend on deposition techniques and processing parameters [4]. In this study, the ion beam sputtering technique was chosen to deposit the ZrN films on the AISI 304 steel substrate. To our knowledge, no reports have been carried out concerning ZrN film formation using this technique. In this work, the influence of $N_2/(N_2+Ar)$ flow ratio ($F(N_2)$) and substrate temperature on the structural and mechanical properties of the deposited films were investigated.

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2. Experimental analysis

2.1. Sample preparation

The quality of the stainless steel 304 substrate with its respective composition, determined by X-ray fluorescence spectroscopy (XRF) is presented in Table 1. The samples ($21 \times 21 \times 2\,mm^3$) were abraded with 1000, 1200 and 2000 grit silicon carbide papers and were given a final polish with 0.03 μm aluminum oxide and ultrasonically cleaned in both acetone and alcohol bath for 5 min and dried with argon.

The coating process is carried out by Kaufman ion source, using ion beam sputtering technique. Pure Ar and N_2 gas were used as the sputtering ions, and their flows were independently controlled by two specific flowmeters: one for argon and another for nitrogen. The working pressure was kept constant at 2.6×10^{-3} Pa and the total flux ($Ar + N_2$) is maintained at 60 sccm. As shown in Fig. 1, the ions of Ar and N_2 were accelerated toward the target (zirconium sheet) with a fixed energy of 2.2 keV and current density of $1.5\,mA/cm^2$ throughout the experiments. The deposition time for ZrN was 4 h in each run. Besides the Ss substrate, a one-side mirror silicon (1 0 0) substrate was used during deposition in order to measure the thickness of the deposited layer. To study the temperature effect, the substrates were heated by means of a resistance heater and a CrNi–Cr thermocouple was used to measure the temperature.

2.2. Characterization techniques

The film thickness was determined by Rutherford backscattering (RBS) spectroscopy of proton at incident energy of 2.1 MeV. The ion beam hits the sample at normal incidence. The scattered particles were measured by a surface barrier detector (detection angle of 165°). Quantitative determination of the film thickness was analyzed using simulation for analysis of materials (SIMNRA and RUMP). The crystallinity and morphology of the films were examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. Furthermore, the chemical composition of the films was determined by energy-dispersive X-ray (EDX) technique. The ZrN, Zr, N, and Fe depth profile were measured by secondary ion mass spectroscopy (SIMS) using Cs^+ as the primary ion beam with accelerating energy of 10 keV. The hardness was measured by Vickers micro-hardness tester using a load of 25 g. To determine the hardness of the films, recognizing the fact that the substrate will influence the measured hardness, Jonsson and Hogmark [8] modeling approach was used. The film hardness is given by

$$H_f = H_s + (H_c - H_s)/[2C_2(t/D) - C_2^2(t/D)^2], \quad (1)$$

where H_s and H_c are the substrate and composite hardness, respectively, $C_2 = 2\mathrm{Sin}^2 11°$, $D = d/7$ (d the measured indentation diagonal), and t is the film thickness in μm.

According to relation (1), an accuracy of 5% has been calculated for the measured hardness.

Table 1
Chemical composition of stainless steel 304

Element	Fe	Cr	Ni	Mn	Si	V	C
atom%	Bal.	18.81	8.98	2.00	0.72	0.17	0.15

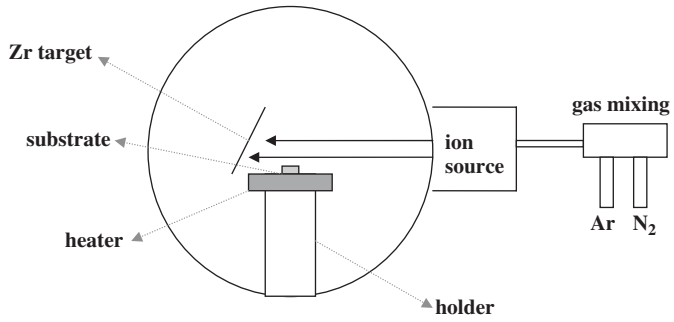

Fig. 1. Schematic of ion beam sputtering deposition arrangement.

3. Results and discussion

The ZrN films thickness was calculated according to RBS results for different $F(N_2)$ values at 400 °C substrate temperature. Table 2 presents the thickness values for different samples as a function of $F(N_2)$. Although the deposition was carried out at the same duration for all samples, the film thickness variations show a large difference ranging from 2.54 to 3.82 μm. It is believed that the lower sputtering yield of nitrogen upon replacing argon can lead partly to a decrease of zirconium sputtered atoms which cause a decrease in thickness. Besides ambient nitrogen from the working gas for operating the ion source, energetic nitrogen particles from the ion beam being backscattered under simultaneous neutralization at the sputter target are very probable to contribute essentially to nitride formation. Resputtering by such particle is expected to reduce the growth rate besides a decrease of the sputtered Zr flow from the target.

Table 3 shows the effect of the substrate temperatures on the ZrN film thickness at $F(N_2) = 10\%$. The thickness

Table 2
Film thickness as a function of the $F(N_2)$ at 400 °C substrate temperature

$F(N_2)$ (%)	Film thickness (μm)
10	3.82
15	3.79
26	3.77
54	3.18
69	2.54