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Hardness and residual stress in nanocrystalline ZrN films: Effect of bias voltage and heat treatment

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ABSTRACT

The purpose of this study was to investigate the effects of both bias voltage and heat treatment on the composition, microstructure, and associated mechanical properties of the zirconium nitride (ZrN) thin films deposited on AISI 304 stainless steel substrates by a filtered cathodic arc ion-plating (FCA-IP) system. The depositions were carried out by varying negative substrate bias voltage, from $-40\,V_b$ to $-80\,V_b$. The deposited film specimens were heat-treated at 800 °C for 1 h. X-ray diffraction (XRD) revealed that (a) texture coefficients of (1 1 1) plane increased with negative bias, and (b) the grain size was approximately less than 15 nm, i.e. nano-scale grain size. The hardness of the deposited ZrN films was correlated with point defects, (1 1 1) texture coefficient, and crystallinity characterized for the films. For the as-deposited films, it was found that the hardness increased with decreasing (1 1 1) full width of the peak at half maximum (FWHM) and increasing (1 1 1) texture coefficient, suggesting a better crystallinity and lower grain boundary mobility in the highly textured films. The decrease in film hardness after heat treatment may be attributed mainly to the reduction of point defects present in the films. Measurements performed for the intrinsic residual stress reported a significant 5.5 GPa release in the heat-treated films, due to recovery of point defects by heat treatment.

1. Introduction

Many transition metal nitrides based on titanium and chromium have stimulated a great deal of commercial interest during the past decade, owing to their attributes such as high hardness, high thermal and chemical stability, and appealing aesthetic color. More recently, ZrN films are getting considerable attentions because of their superior mechanical properties [1,2], golden color [3], various applications such as diffusion barriers in the microelectronic industry [4,5], and protection layer used in the fission reactors [6]. However, since zirconium has a higher melting point, a lower vapor pressure, and higher contamination susceptibility by oxygen and carbon, successful deposition of decent quality ZrN film poses greater difficult than TiN or CrN films. As such, only few studies on ZrN film were reported, comparing with other nitride films.

One of the most critical parameters involved during the growing thin film is the substrate bias. The negative bias applied on the substrate influences kinetic energy and momentum of the charged particles delivered to the growing film by accelerating the particles. Therefore, the corresponding microstructure such as preferred orientation, grain size, and point defects of the film may vary as well. Film hardness, the capability of resistant to deform, affected by the microstructure, is a major index of the mechanical properties.

The grain size may play a significant role in the deformation mechanisms of materials. The plastic deformation of mesograin (>100 nm) material is based on dislocation slip via slip systems; while for nanograin (<100 nm) material, it was proposed [7–9] that the dominant deformation mechanisms of thin film may involve the grain rotation and grain boundary slide. Earlier studies reported that nanohardness of TiN film would be increased with an increasing (1 1 1) texture coefficient [10,11]. It implies that the effect of (1 1 1) texture coefficient on nanohardness of films may not be ignored. However, the rationalization of this behavior may cause some difficulty via dislocation theory. In addition to grain size and preferred orientation, our recent study [12] suggested that point defects produced during deposition is a major contributing factor to hardness of films, where the defect density was significantly reduced by heat treatment, with an accompanying decrease of film hardness. Those findings reported in the preceding literature indicated that complicated interactions are involved in the factors that affect the film hardness. However, no definite knowledge has yet been established regarding the interplay of preferred orientation,

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nano-scale grain size, and point defects, with the hardness of the nanocrystalline thin film.

Heat treatment processes have been widely employed to improve the properties of hard coating through reducing the residual stress and defects [12–14]. The hardness of nitride hard coatings subject to heat treatment has been reported with quite different results [13,14]. In a study by Mader et al. [13], they reported a significant drop of the film hardness and proposed a softening mechanism, which rationalized that the massive point defects would form voids at grain boundary. However, in a study by Chou et al. [14], they found that the heat-treated specimens had 10–30% higher hardness than the as-deposited specimens without a significant change of microstructure or packing factor. Therefore, the softening mechanisms involved in heat treatment, which may influence the film's microstructure and properties, are not entirely understood. Moreover, it is not clear whether heat treatment can play a similar role on the hardness and residual stress on the texture development of ZrN films at a higher stress state such as higher than 10 GPa in ZrN films.

This study was motivated to investigate the effects of the bias voltage applied on the substrate and the post-deposition heat treatment on the composition, the structures, and the mechanical properties of the nanocrystalline ZrN films deposited on stainless steels substrates by the filtered cathodic arc ion-plating (FCA-IP) device.

2. Experimental procedures

ZrN films were deposited using FCA-IP method. A classical 90°-duct filter was adopted to filter out the macroparticles generated along with plasma flux. The substrate used in the study was a 304 stainless steel. Before coating, the specimens underwent progressively an ultrasonic cleaning process, which used acetone and ethanol and then dried in a vacuum dryer. The specimens were heated in the coating chamber that had been evacuated to about 1.3×10^{-3} Pa, until the temperature of the environment reached 365 °C. After the arc was initiated by a trigger, local melting at the Zr target surface took place, forming an arc spot on the Zr target. Constant nitrogen partial pressure of 2.7×10^{-2} Pa was kept during coating. Meantime, Ar gas flow of 1 sccm was also introduced to stabilize the plasma. The film deposition time was 15 min for preparing all the specimens. After deposition, heat treatments were performed for the films deposited. A Lingberg high temperature tube furnace equipped with a mechanical pumping system was used for the heat treatments. Our previous study [12] has developed a standard heat treatment procedure to prevent the oxidation of thin film by a controlled atmosphere and using Ti oxygen getter. Heat treatment was performed at 800 °C/1 h.

Crystal structure and preferred orientation of the ZrN films were characterized by X-ray diffraction (XRD). The extent of (1 1 1) preferred orientation is quantified by a texture coefficient defined as $I(1\,1\,1)/[I(1\,1\,1)+I(2\,0\,0)+I(2\,2\,0)]$, where I is the integrated intensity of the corresponding Bragg peak. The position of the (1 1 1) diffraction peak and the full width of the peak at half maximum (FWHM) were used to estimate the grain size by Scherrer's equation [15].

Thickness of ZrN films were measured employing a Secondary Ion Mass Spectroscopy (SIMS) instrument. Rutherford Backscattering Spectrometry (RBS) was used to determine N/Zr ratios of the ZrN films. N/Zr ratio was obtained through spectrum analysis using the Rump simulation code. The film hardness was measured by a Digital Instrument atomic force microscope equipped with Hysitron nanoindenter. The procedures of applying load and calibration of the nanoindenter were detailed in our previous paper [11]. The hardness was calculated using Oliver–Pharr technique [16], which could be executed from the software provided by Hysitron Inc. The average value of the 10 indentations made for the nanohardness measurement was reported. The residual stress of ZrN films was determined by a modified XRD $\sin^2\psi$ method using a four-circle diffractometer with psi-goniometer geometry [17]. In order to increase the diffraction volume of the thin film specimen, an incidence grazing angle of 2° was used in the X-ray tests. The (2 2 0) peak of ZrN films was found to be the one with the weakest oscillation and also provided sufficient intensity for precisely determining the peak position.

3. Results and discussion

3.1. Microstructure

The effects of negative substrate bias and heat treatment on the microstructure of ZrN films deposited by filtered cathodic arc ion-plating system are characterized by X-ray diffraction. Fig. 1(a) shows the diffraction peaks of crystalline ZrN, demonstrating a strong dependence of film texture on the negative bias voltage applied to the substrate. Noting that with increasing negative bias, the increase in diffraction intensity of (1 1 1) preferred orientation was found; the corresponding (1 1 1) texture coefficient listed in Table 1 also increases. Theoretically speaking, (2 0 0) plane has the

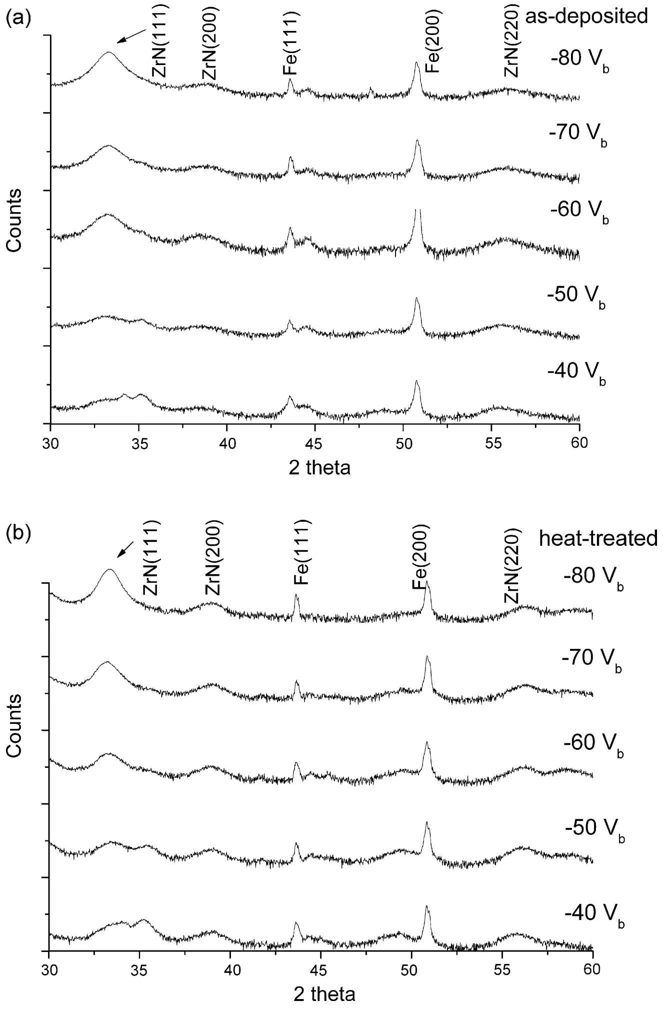

Fig. 1. XRD patterns of (a) as-deposited films and (b) heat-treated films with varying negative substrate bias.