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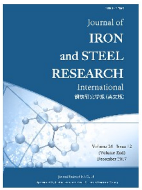

Influence of bias voltage on structure, mechanical and corrosion properties of reactively sputtered nanocrystalline TiN films

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ABSTRACT

Nanocrystalline TiN films were prepared by DC reactive magnetron sputtering. The influence of substrate biases on structure, mechanical and corrosion properties of the deposited films was studied using X-ray diffraction, field emission scanning electron microscopy, nanoindentation and electrochemical techniques. The deposited films have a columnar structure, and their preferential orientation strongly depends on bias voltage. The preferential orientations change from (200) plane at low bias to (111) plane at moderate bias and then to (220) plane at relatively high bias. Nanohardness H, elastic modulus E, H/E^* and H^3/E^{*2} ratios, and corrosion resistance of the deposited films increase first and then decrease with the increase in bias voltage. All the best values appear at bias of −120 V, attributing to the film with a fine, compact and less defective structure. This demonstrates that there is a close relation among microstructure, mechanical and corrosion properties of the TiN films, and the film with the best mechanical property can also provide the most effective corrosion protection.

1. Introduction

TiN films are widely used as protection coatings of cutting tools, molds and dies against abrasion, corrosion and oxidation[1,2]. They are generally produced by physical vapor deposition (PVD), and the relationship between depositing processes, microstructure and properties is investigated[3-6]. The mechanical properties and corrosion resistance of the sputtered films are strongly dependent on their microstructure affected by processing parameters[7-10]. In general, TiN films are inert and stable in most aggressive media. However, PVD films most often present growth related defects such as pinholes and pores, through which the substrate materials are attacked in corrosion media[11-13]. Therefore, for industrial applications, PVD films with a fine, homogeneous and compact structure are always desirable, especially for promoting corrosion resistance.

Although there has been much information about microstructure, mechanical and corrosion properties for PVD metal nitride films[14-16], it is not always consistent due to various processing parameters used. The films which have the best mechanical properties are mostly not with the best corrosion resistance[14,16] because their corrosion resistance is very sensitive to the pores or pinholes[13,17]. Moreover, previous researches have shown that the microstructure and properties of TiN-based multilayer films (e. g. TiN/Ti[14], TiN/AlN[18], TiN/CrN[19], TiN/ZrN[20], TiN/W_2N[21], TiN/TiAlN[22], etc.) are associated with the TiN single layer. Therefore, it is also important to prepare a monolithic TiN film with high quality in multilayer systems[6,21,23]. In this paper, nanocrystalline TiN thin films were prepared by DC reactive sputtering at various bias voltages, and the relationship among bias, structure, mechanical and corrosion performance of the resulting films was studied in detail. The results show that PVD film produced at a proper bias voltage can exhibit both high mechanical and corrosion performance due to its fine, dense and less defective structure, which is very useful for the application of nitride-based films in abrasive and corrosion protection fields.

2. Materials and Methods

2.1. *Film preparation*

Nanocrystalline TiN thin films were prepared on

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both Si (100) and 304 stainless steel substrates using DC reactive magnetron sputtering. The apparatus schematic diagram is presented in Fig. 1. The distance of the Ti (99.99%) target to the substrate was about 8 cm. The substrate was successively cleaned for 20 min in acetone, 10 min in ethanol and 5 min in deionized water by ultrasonic wave. The base and working pressures of the deposition chamber were 6.0×10^{-4} Pa and 0.5 Pa, respectively. Ar (99.999%) and N_2 (99.999%) gases were used with fixed flow rates of 30 mL/min and 4 mL/min, respectively. Ti thin interlayer was first deposited on the substrate in Ar gas atmosphere for 10 min to promote adhesion, and then the TiN layer was deposited atop in a mixture atmosphere of Ar and N_2 gases for 2 h. The bias voltage applied on the substrate changed between −50 and −155 V. During deposition, the substrate was kept at 300 ℃.

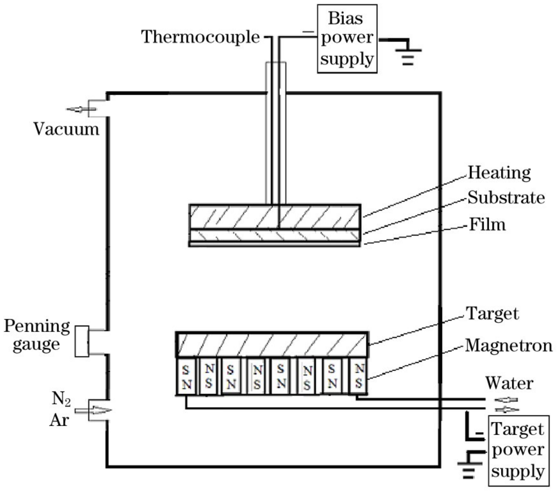

Fig. 1. Schematic diagram of experimental apparatus.

2.2. Film characterization

The film microstructure was examined by field emission scanning electron microscopy (FESEM S4800). The phase composition was characterized by X-ray diffraction (XRD, PANalytical B. V. X Pert Pro MPD) with CuKα radiation (wavelength of 0.15406 nm) operated at 40 kV and 40 mA. The grazing incident angle was 2°, the scanning angular (2θ) scope was 30°−90° and the scanning rate was 2(°)/min. Nanohardness and elastic modulus were measured by MTS XP nanoindenter system equipped with a Berkovich diamond indenter under 2 mN peak load, and mean values were obtained based on 5 indentations. The ratio of indentation depth/film thickness was no more than 0.1 in order to avoid the substrate effect.

Corrosion resistance was evaluated at 25 ℃ in 3.5% NaCl aqueous solution using PARSTAT 2273 advanced electrochemical system. The reference and auxiliary electrodes were a saturated calomel electrode and a graphite bar, respectively. Before measurements, the TiN specimens were put into the electrolyte solution until a steady open circuit potential (OCP) was recorded. Polarization curves were measured with a potential scanning rate of 0.332 mV/s, and electrochemical impedance spectroscopy (EIS) was recorded at OCP in frequency range between 10^5 Hz and 1 mHz by stimulating the specimens with an AC signal of 10 mV. The specimens were covered with electrical insulating paraffin except the surface for electrochemical measurements.

3. Results and Discussion

3.1. Microstructure

Fig. 2 presents the surface morphologies of the TiN films produced under different negative biases. It can be seen that the surface microstructures strongly depend on the biases, and both the surface roughness and compactness are improved when the negative bias increases from −50 to −120 V. However, too high negative bias (−155 V) may degrade the compactness and roughness as shown in Fig. 2 (d) where some voids appear, arising from the ion bombardment effect on the surface mobility of adatoms. Some crystallites grow in the form of trigonal pyramids as well as relatively flat particles on the −50 V biased film surface (Fig. 2(a)), leading to a very rough surface with pinholes. This is in agreement with Ref. [5]. Obviously decreased microstructural defects and improved roughness with increasing negative bias voltages will improve film properties, especially corrosion resistance[13].

Fig. 3 shows the cross-section structures of the TiN thin films produced at different biases. The TiN thin films have a columnar structure. The average diameter of the columns decreases and the compactness is improved when the bias voltage increases. The column diameter appears to be finer at the film/substrate interface and enlarges slowly with increasing the distance from the interface. Similarly, the compactness is higher near the interface (Fig. 3).

Fig. 3 also shows the film thickness changes with bias voltage, which is closely related to the sputtering process[3]. Under lower bias voltage, the ion current density increases with increase in bias voltage; therefore, the film thickness increases from 0.77 μm at −50 V to its maximum value of about 1.01 μm at −85 V. Further increasing bias voltage can enhance re-sputtering effect which can hinder the film growth[7,8], causing almost no change in the film thickness with bias voltage between −85 V and −120 V. When the bias voltage further increases, the re-sputtering effect becomes remarkable and finally leads to obviously decreased film thickness (0.88 μm at −155 V).