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Effect of structural defects on corrosion initiation of TiN nanocrystalline films

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ABSTRACT

TiN thin films were deposited on AISI304 stainless steel using a DC reactive magnetron sputtering process. An in situ observation is carried out in order to investigate the relationship between the corrosion initiation and the structural defects such as pores and pinholes by using atomic force microscopy (AFM). It is found that the corrosion initiates at some larger structural pores in the form of the detachment of the particles which will plug the transport path for the corrosion products, whereas the small enough pinholes are easily filled in by corrosion products at the beginning of corrosion. Also, the surface roughness of the corroded film is improved with increasing the corrosion time. The corrosion morphology after polarization test shows that fewer and large pits appear on the TiN-coated substrates probably associated with large structural defects such as high density area of through film pores or pinholes present in the films, which is in accord with those results obtained by in situ AFM observation. Additionally, the effect of bias voltages on corrosion resistance of the films is also involved because the structural defects are strongly associated with the bias voltages.

1. Introduction

TiN thin films have been serving the industry as wear resistance, corrosion resistance, diffusion barriers and decorative coatings due to their high hardness, high wear resistance, chemically stability and beautiful color [1]. These films can be prepared by several PVD techniques such as ion-beam deposition, cathodic-arc deposition and reactive sputtering. Among them, a considerable number of studies have been performed in reactively sputtered TiN in order to investigate the relationship between deposition parameters, film structure and the final properties of the material [2–5]. The mechanical and corrosion properties of thin films prepared by magnetron sputtering strongly depend on their microstructural characteristics, which are greatly affected by the processing parameters [6–9]. For example, a negative bias voltage applied to the substrate can significantly improve the ionization and energy of the sputtered particles and enhancing the film crystallization. Therefore, film homogeneity and compactness increase with increasing substrate bias voltages in a certain range, resulting in increases in hardness, Young's modulus, load capacity, toughness [6], and compressive residual stress [4], and improvement in corrosion resistance [9] and antioxidation [3]. Generally, TiN coatings are chemically inert and thermally stable, but PVD coatings most often exhibit growth related defects, e.g. pores and pinholes, through which a corrosion attack on the substrate materials takes place [10–12]. Therefore, in order to gain excellent performance from PVD coatings, a fine, dense and uniform coating structure is always desirable, particularly for the improvement of corrosion resistance.

Although there are increasing reports about corrosion behavior of TiN thin films produced by reactive magnetron sputtering, the results are not always in accordance with each other due to using different processing parameters, and an in situ observation on the effect of structural defects on corrosion behavior of the film is not found although more researchers consider that the structural defects are responsible for the corrosion initiation. In the present work, TiN thin films were prepared by DC reactive magnetron sputtering, and an in situ AFM observation is carried out in order to find out the relation of structural defects and corrosion initiation at the beginning of corrosion. Additionally, the effect of bias voltages on corrosion resistance of the films is also involved in the present study because the structural defects are strongly associated with the bias voltages.

2. Materials and methods

TiN films were deposited on AISI 304 stainless steel substrate with dimensions of 25 mm × 25 mm × 2 mm by using DC reactive magnetron sputtering. Titanium (99.99% in purity) target of

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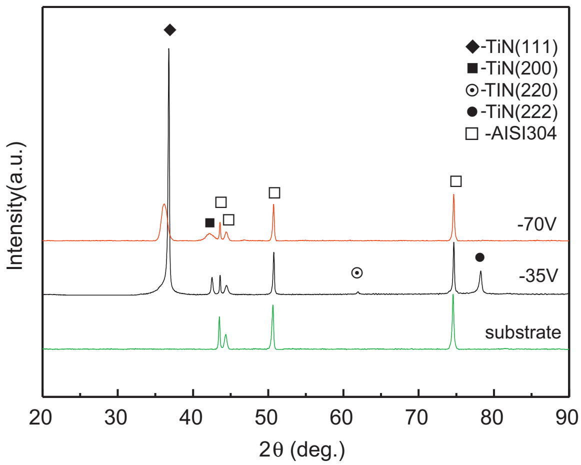

Fig. 1. X-ray diffraction results for the TiN thin films deposited at different bias voltages.

diameter 60 mm and thickness 4 mm was mounted about 80 mm below the substrates. The substrate was ultrasonically cleaned for 20 min in acetone followed by 10 min ultrasonic cleaning in ethanol and finally 5 min ultrasonic cleaning in deionized water. The base pressure of the deposition chamber was pumped to 6.0×10^{-4} Pa and the process pressure was fixed at 0.5 Pa. High purity working gas, Ar (99.999% in purity), and reactive gas, N_2 (99.999% in purity), were used; their flow rates were regulated by mass flow controllers. Ar and N_2 gas flow rates were fixed at 30 sccm and 4 sccm, respectively. A thin Ti interlayer was incorporated between the substrate and the film for improved adhesion [13]. Argon plasma was first used for the Ti interlayer with a deposition time of 10 min and then a mixture of argon plus nitrogen for the TiN layer with a deposition time of 120 min at different substrate bias voltages (V_b). Our experimental results have shown that relative high defects appear in the TiN films produced at $|V_b| \leq 50$ V, whereas fewer defects were found with the film at $|V_b| \geq 70$ V [14]. In the present study, we only present the films produced at $|V_b| < 50$ V and $|V_b| = 70$ V. During the deposition, the substrate was cooled through flowing water.

An in situ observation on corrosion morphology was carried out in 3.5% NaCl at room temperature by using AFM (Agilent 5500) in tapping mode, and root mean square roughness of the corroded film was calculated. The microstructure of the TiN thin films was observed using field emission scanning electron microscopy (FESEM S-4800, Hitachi). The crystal structure was analyzed using X-ray diffraction with a Cu-K_α 40 kV/30 mA X-ray source (wavelength $\lambda = 0.15406$ nm).

Potentiodynamic polarization measurements were made at 25 °C in a three-electrode cell containing 3.5% NaCl aqueous solution by using PARSTAT 2273 advanced electrochemical system. A saturated calomel electrode (SCE) was used as the reference electrode, and the counter electrode was graphite. The scanning started from −250 mV versus the open circuit potential and ended after a whole polarization curve was obtained. The scanning rate was 0.332 mV/s.

3. Results and discussion

Fig. 1 presents the XRD analysis results of the TiN thin films produced at −35 V and −70 V bias voltages, respectively. The peaks around 43.6°, 44.3°, 50.7° and 74.6° are from the AISI 304 stainless steel substrate underneath the films. All the other peaks are attributed to (1 1 1), (2 2 0), (2 0 0) and (2 2 2) diffraction planes of TiN films, exhibiting a dominant orientation of the (1 1 1) plane. The (1 1 1) preferential orientation is possibly due to the smallest surface energy storage in the stressed state. As a consequence of enhanced mobility of atoms on the growing film surface, the film structure can be relaxed to a lower energy state with the formation of (1 1 1) texture [6].

The average grain size can be estimated by the Debye–Scherrer formula [15]:

$$D = \frac{K\lambda}{\beta\cos\theta} \tag{1}$$

where K is a constant ($K = 0.91$), D is the mean crystalline dimension normal to diffracting planes, λ is the X-ray wavelength ($\lambda = 0.15406$ nm), β in radian is the peak width at half-maximum height and θ is the Bragg's angle. The calculated grain sizes of the TiN crystallite are 36.1 nm and 11.0 nm for the −35 V and −70 V biased films, respectively. The smaller grain size for larger bias voltage is perhaps contributed to the penetration of impinging ions into the lattice of the condensed film and the increased generation of defects which will lead to an increased number of preferential nucleation sites, resulting in smaller grains [6,16].

Fig. 2 shows the surface and across sectional morphologies of TiN thin films prepared at biases of −35 V and −70 V, respectively. The morphologies are totally consistent with the results reported by Su et al. for the films produced under similar conditions [17]. The surface microstructures are strongly dependent on the bias voltages applied, and improved rough and compact surfaces are gained as the bias voltages increase [14]. This difference in morphology is thought to be due to the ion bombardment effects on the surface mobility of just deposited atoms [6]. The grain sizes of the films obviously decrease as the bias voltage increases from −35 V to −70 V. The crystallites grown at −35 V bias voltage terminate at the surface in the form of trigonal pyramids (Fig. 2a), resulting in a very rough surface [5]. The across sectional morphologies show that the films have columnar structure. Generally, columnar structure is the typical structure for TiN films prepared by DC reactive magnetron sputtering [11,17,18]. The thickness of the −35 V and −70 V biased films is 1063 nm and 875 nm, respectively (Fig. 2). The decrease in the deposition rate with increasing bias voltage would be related to the ion-peening effect and subsequent re-sputtering of the film, in detriment of thickness increase [7,8]. The TiN films exhibit the columnar structure with pores and pinholes between the inter-granular column [11,17,19], forming a direct path for the corrosive medium to pass through the film defects [18].

Because the corrosion resistance of the film is dependent on the structural defects [19,20], in order to find out the relationship between the microstructure and corrosion initiation, an in situ observation was carried out by using AFM working at tapping mode in 3.5% NaCl at room temperature, and the evolution of corrosion morphology of the TiN film deposited at −45 V bias voltage with scanning time is shown in Fig. 3. The scanning continuously runs, lasting about 12 min to complete each image. The film was immersed in the 3.5% NaCl solution about 10 min before starting the scanning. It is clearly shown that an interaction appears between the structural defects such as pores and pinholes and the corrosion media. For larger pores (marked as 1 and 2) in Fig. 3a, they become larger and larger as the scanning progresses, and one crystalline particle is found to fall off the boundary of pore 2 after approximately 28 min scanning (Fig. 3b), 3–5 crystalline particles at the boundary of pore 1 fall off one after the other after approximately 30 min (Fig. 3b) and 68 min (Fig. 3c) scanning. This indicates that the crystalline particles located at the boundaries of the pores are weakly bonded; they easily fall into the pores when corrosion media attacks their grain boundaries, showing that the larger pores may be the most possible spots for corrosion initiation. When the attacked pores grow, more stainless steel substrate will be exposed to the corrosion media, leading to accelerated corrosion due to localized galvanic corrosion at the TiN/substrate interface [21,22].