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Microstructures and properties of titanium nitride films prepared by pulsed laser deposition at different substrate temperatures

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ABSTRACT

The nanostructured titanium nitride (TiN) films were fabricated by pulsed laser deposition (PLD) technique at different substrate temperatures under residual vacuum, and the influence of substrate temperatures on the microstructure, mechanical and tribological properties of TiN films was investigated and discussed. The results shown that the consistent stoichiometric TiN films were obtained and the grain size increased from 10.5 to 38.7 nm with the increasing of substrate temperature. The hardness of films decreased with the substrate temperatures increasing, the highest hardness reached to 30.6 GPa at the substrate temperature of 25 °C, and the critical load increased first and decreased at 500 °C, the highest critical load was 23.8 N at the substrate temperature of 300 °C. The film deposited at the substrate temperature of 25 °C registered the lowest friction coefficient of 0.088 and wear rate of 7.8×10^{-7} $mm^3/(N\,m)$. The excellent tribological performance of the films was attributed to the small grain size, high hardness and smooth surface of the film.

1. Introduction

As a transitional metal nitride, titanium nitride (TiN) has been exploited systematically in applications for hard and protective films due to its excellent properties such as outstanding hardness, high strength and rigidity, good stability at high temperatures and excellent wear resistance [1,2]. In the past few decades, many researchers have studied the TiN films by a variety of film deposition techniques, including the physical vapor deposition (PVD) [3], chemical vapor deposition (CVD) [4,5], magnetron sputtering (MS) [6–10], ion implantation [11,12], thermal spraying [13,14] and so on. Compared with above methods, the pulsed laser deposition (PLD) technique [15–17] has proven to be rapid, efficient, easy operation and cost-effective in the fabrication of high-quality thin films. It is a kind of physical vapor deposition technique which has controllable deposition parameters, including laser energy, repetition rate, substrate temperature, deposition time, gas flux as well as target–substrate distance. Growth conditions such as deposition atmosphere [18,19], repetition rate [20] and substrate temperature [21–23] can hugely modify the crystalline quality, microstructure, thickness, surface morphology and mechanical properties of films, which have been investigated in great detail. In previous study, Lippert [21] used the PLD technique to fabricate the yttria-stabilized zirconia (YSZ) films at room and high temperatures, which exhibited a uniform isotropic structure in the case of room temperature deposition and an oriented columnar growth at substantially higher substrate temperatures of 400–700 °C. Matei [23] fabricated the vanadium nitride films at room temperature and 500 °C by the PLD technique. They found that the substrate temperatures greatly influenced the thickness of the films which was higher when the films were obtained at 500 °C (30 nm) compared to room temperature (17 nm), and the surface roughness value increased from 0.37 to 0.46 nm with the raising of substrate temperature. The substrate temperature can effectively and directly enhance the ad-atom mobility through the temperature-dependent thermal vibration [24,25], hugely modify the crystalline quality, microstructure and surface morphology evolution of the thin films, fundamentally influence the mechanical properties of films.

However, to the best of our knowledge, the investigations on the growth conditions, such as substrate temperatures, of TiN films deposited by PLD technique are really rare. Moreover, most of the TiN films were deposited under N_2 or Ar + N_2 atmosphere using Ti target to obtain the chemical-reacted TiN phases in literatures, while in present work, the standard stoichiometric TiN films were

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deposited by PLD at different substrate temperatures under residual vacuum using TiN target directly, and we reported the first time for the effect of substrate temperatures on the microstructures and properties of TiN films scientifically. It is expected that the consistent stoichiometric nanostructured TiN films with satisfied mechanical and tribological properties could be fabricated by controlling the depositing substrate temperatures and the potential application of TiN films as anti-wear and protective coating.

2. Experimental details

2.1. Films preparation

The films were deposited by PLD technique using a KrF excimer laser (λ = 248 nm, pulse duration = 25 ns, COMPexPro 205) to ablate the TiN target with the dimension of Φ60 mm × 5 mm and 99.99% purity. The deposition chamber was evacuated by a mechanical pump and the molecular pumping to 6.0×10^{-5} Pa prior to ablating the target. The deposition parameters were as follows: laser energy = 400 mJ, repetition rate = 10 Hz, 36,000 pulses for each sample. The films were deposited on silicon wafer at nominal substrate temperatures of 25 °C, 100 °C, 300 °C, 500 °C, and then the samples were denoted as TiN1, TiN2, TiN3, TiN4, respectively. The silicon wafer was ultrasonically cleaned with acetone and alcohol and deionized water for 20 min, dried with pure nitrogen before placed to the substrate holder. The target was placed parallel to substrate at a distance of approximately 50 mm. Both the target and the substrate were cleaned with argon plasma for 30 min. The target rotated at a speed of 15 rpm during the laser ablating in order to avoid the formation of deep craters, and the substrate rotated at a speed of 10 rpm to obtain uniform films.

2.2. Films characterization

Crystalline quality, mass density and grain size of the films were identified by means of X-ray diffraction (X'Pert-MRD, Philips, Cu Kα radiation, λ = 0.154056 nm) technique at a potential of 40 kV and current of 60 mA, the scanning range of 2θ was from 25° to 80°, at the grazing incidence angle of 1–5° differently. The data were analyzed with Jade 6.0 software and peaks were identified by comparing with standard ICSD patterns (89/54378) data files. The crystallite size of the films was calculated by the Scherrer equation and Williamson–Hall plot method [18].

The surface morphologies of the films were characterized by atom force microscope (AFM, AIST-NT Smart SPM, USA) with a conventional rectangular cantilever (tip curvature ≤10 nm). The thickness of the films was determined by ellipsometer (L116E, Gaertner, USA), which was equipped with a He–Ne laser (632.8 nm) set at an incident angle of 50°. The refraction coefficient of silicon was set as 3.85, extinction coefficient was 0.02*i*. Ten points along the diameter of the substrates were taken, and the average value of film thickness was reported.

Micro-hardness and elastic modulus of the films were measured using in situ nanomechanical testing system (TI950, Hysitron TriboIndenter, USA) with a cube-corner diamond tip and set to run five indents on each sample. In order to exclude the influence of substrates, the nanoindentation experiments were performed in displacement control with a contact depth up to 100 nm. Hardness and elastic modulus were determined from the load displacement data following the model of Oliver and Pharr [26].

The adhesion strength was tested by a conventional scratch method using a Rockwell penetrator (diameter = 200 μm). Scratch test was driven across the films at a linear increase of the load from 0.03 N up to 50 N in 1 min and the scratch length was 4 mm. At least five scratches were done for each sample and adhesion strengths were obtained by averaging the five different scratch tests. The force correspond to the delamination of the film and was referred to as critical load (Lc) and was determined by correlation of three methods of observations: changes in the friction coefficient as a function of scratch length, changes in the penetration curves as a function of scratch length and microscopic observations [22].

The friction and wear performances of the films were conducted by a ball-on-disk tribometer (UMT-3, Bruker). The disk was the TiN film, and the pair part was Al_2O_3 ceramic ball (3 mm in diameter). The tests were run at the normal load of 2 N, the sliding velocity of 0.02 m/s, the sliding distance of 50 m at room temperature in atmosphere with a relative humidity of 40 ± 5%. The wear volume loss was evaluated by a NanoMap 500LS three-dimensional (3D) surface profiler with a stylus tip in tapping mode. The wear rates (K_W) were calculated using the equation of $K_W = V_W/(P \times L)$, where V_W is the wear volume loss in mm^3, P is the normal load applied in N, and L is the sliding distance in meter (m).

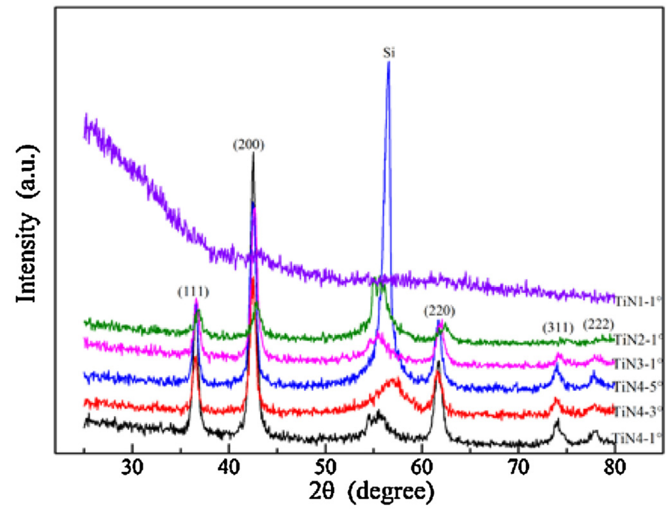

Fig. 1. GIXRD patterns of the TiN films deposited at different substrate temperatures.

3. Results and discussion

3.1. GIXRD analysis

Fig. 1 presents the grazing incidence X-ray diffraction (GIXRD) patterns of TiN films deposited at different substrate temperatures, indicating that the consistent stoichiometric titanium nitride films were obtained. It can be seen that the TiN films are highly oriented in [2 0 0] orientation only when deposited at a substrate temperature of 25 °C. As the substrate temperature increasing, the additional randomly oriented grains could be observed, the [1 1 1], [2 2 0] peaks appears at the substrate temperature of 100 °C, and the [3 1 1], [2 2 2] appears at the substrate temperature above 300 °C. However, the preferential [2 0 0] peak remains the strongest line, indicating it retains the largest volume fraction. The preferred orientation observed in the films as a function of the deposition temperatures can be explained by considering the competition between surface energy and epitaxy in accordance with Krzanowski's work [16], where the TiN films shown a strong [2 0 0] orientation at all temperatures with additional grain orientations present at 400 and 600 °C. This result is also similar to the TiN film deposited at the temperature of 700 °C, where the strongest TiN [2 0 0] peak is clearly observed [17]. Owing to TiN has a B1 structure with low energy [1 0 0] planes, surface energy effects dominate leading to [2 0 0] oriented films at low temperatures. At higher temperatures, with higher atomic mobility, there is more of a tendency