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Effect of the microstructure of Si_3N_4 on the adhesion strength of TiN film on Si_3N_4

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Abstract

The effect of the microstructure of silicon nitride, which was used as a substrate, on the adhesion strength of physical vapor deposited TiN film on Si_3N_4 was investigated. Silicon nitride substrates with different microstructures were synthesized by controlling the size (fine or coarse), the phase (α or β) of starting Si_3N_4 powder, and sintering temperature. The microstructure of Si_3N_4 was characterized in terms of grain size, aspect ratio of the elongated grain, and β-to-α phase ratio. For a given chemical composition but different mechanical properties, such as toughness, elastic modulus, and hardness of Si_3N_4 were obtained from the diverse microstructures. Hertzian indentation was used to estimate the yield properties of Si_3N_4, such as critical loads for yield (P_y) and for ring cracking (P_c). The effect of the microstructure of Si_3N_4 on adhesion strength evaluated by scratch test is discussed. TiN films on Si_3N_4 showed high adhesion strengths in the range of 80–140 N. Hardness and the P_y of Si_3N_4 substrate were the primary parameters influencing the adhesion strength of TiN film. In TiN coating on Si_3N_4, substrates with finer grain sizes and higher α phase ratios, which show high hardness and high P_y, were suitable for higher adhesion strength of TiN film.

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1. Introduction

TiN coatings have a high elastic modulus, hardness, good wear resistance, and a low frictional coefficient. These characteristics enable TiN to be applicable as protective and functional coating to increase the life of machining tools [1–5] or to diffuse or act as an oxidation barrier in semiconductor devices [6–8]. Strong adhesion is necessary to obtain high performing TiN. A number of factors have been found to influence adhesion strength between the coating and substrate in Physical Vapor Deposition system. These include coating thickness, substrate hardness, internal stress, and so on [9–15].

Silicon nitride is one of the most successful structural ceramics over the last two decades. Silicon nitride possesses well-balanced mechanical properties, such as a high strength of up to 1 GPa, a high elastic modulus of 330 GPa, and a hardness of 23 GPa. The properties of Si_3N_4 strongly depend on its microstructure, in terms of grain size, β-to-α phase ratio, aspect ratio of elongated β grains, and grain boundary second phase [16–19]. The major application fields of Si_3N_4 have been engine components and cutting tools, and have recently extended to the bearings for high speed or severe environments [20]. However, the relatively high frictional coefficient and high manufacturing cost of Si_3N_4 bearings limit a wider application to various fields.

In this study, as a representative of hard coating material, TiN coatings have been coated on Si_3N_4 by the PVD process, and the adhesion strength of the TiN film was characterized. Previously, TiN dispersed Si_3N_4 composites have been studied [21–23], but TiN coated Si_3N_4 has rarely been reported. In this work, the effects of the microstructure of Si_3N_4 substrate on the adhesion strength of PVD TiN coating on Si_3N_4 were investigated. Silicon nitride substrates with different microstructures but the same composition were fabricated by controlling the size and the phase of the Si_3N_4 starting powder and sintering

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temperature. This study aims to propose the optimum Si_3N_4 microstructure for the best performance of TiN coated Si_3N_4 for various applications including bearings.

2. Experimental details

Physical vapor deposited TiN films on Si_3N_4 ceramic substrates were fabricated, the properties of the substrate and TiN film were evaluated, and adhesion strengths were measured, as indicated in Fig. 1. For the preparation of the ceramic substrate, three kinds of Si_3N_4 powder were used: 0.3 μm fine powder with α phase (UBE-SN-10, Tokyo, Japan), 1.0 μm coarse powder with α phase (UBE-SN-E3, Tokyo, Japan), and 3.0 μm β powder (KSN-80SP, ShinEtsu, Tokyo, Japan). As sintering additives, 5 wt.% Y_2O_3 (Fine Grade, H.C. Starck GmbH, Goslar, Germany), 2 wt.% Al_2O_3 (AKP50, Sumitomo Chemical Co. Ltd., Tokyo, Japan), and 1 wt.% MgO (High Purity, Baikowski Co., NC, USA) were added to the powder mixture. Ball milling was carried out for 24 h with a ZrO_2 ball in 2-PrOH to obtain uniform mixing. After drying in a convection oven at 50 °C for 6 h, the mixed powders were granulated by sieving with a 60-mesh screen.

Hot pressing (Thermal Technology Inc., ASTRO group 1400, CA, USA) was conducted to sinter Si_3N_4 powder under the conditions of the uniaxial compression of 25 MPa in a 1 atm N_2 atmosphere at 1600, 1700, and 1800 °C for 1 h. The heating rate was 25 °C/min and temperature was measured by pyrometer (TR-630A, Minolta, Japan). The sintered specimen was 20 mm in diameter and 3 mm in thickness. After successive polishings with 6, 3, and 1 μm diamond paste, Si_3N_4 was plasma etched to observe its microstructure. During plasma etching, the flow rate of CF_4, and O_2 was 40 and 80 sccm, respectively. A chamber pressure of 34.55 Pa was maintained, and 80 W of RF power was applied for 10 min. The average size and aspect ratio of Si_3N_4 grains were measured by an image analyzer (Bioscan OPTIMAS 4.1, Bioscan Inc., Edmonds, WA, USA). The phase ratio of β-to-α was determined by relative peak intensity ratio obtained from α and β phase according to Gazzara and Messier procedure [24], and density was measured by Archimedes method.

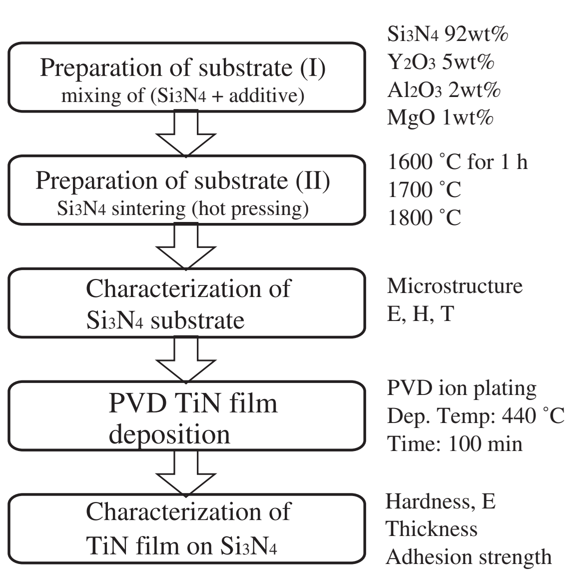

Fig. 1. The flow chart of synthesis of Si_3N_4 substrates and deposition of the PVD TiN film on Si_3N_4.

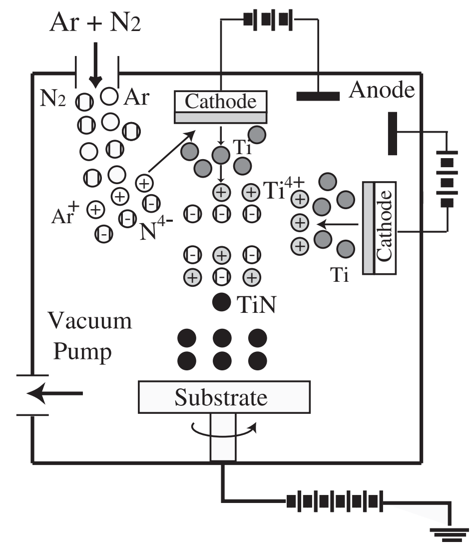

Fig. 2. The schematic design of the cathodic arc ion plating system for TiN deposition. Substrate holder was rotated at a speed of 5 rpm to get uniform TiN thickness on the whole substrate area.

Elastic modulus of Si_3N_4 was evaluated by the impulse excitation of vibration [25], and fracture toughness was obtained by measuring the length of radial cracks after Vickers indentation [26]. A Hertzian indentation with a WC spherical ball of 1.98 mm in radius was introduced on a polished Si_3N_4 surface to determine the critical load for yield P_y, and the critical load for ring cracking, P_c. The critical load for yield is defined as the initial load for inducing surface indentation impression [27]. Load was applied from 700 to 3000 N at an interval of 100 N, and cross-head speed remained constant at 0.5 mm/min. After indentation, the surface of the Si_3N_4 was examined by optical microscopy with Nomarski illumination.

The TiN was deposited by arc ion plating. Fig. 2 shows the schematics of arc ion plating equipment. Before placing in the deposition chamber, the Si_3N_4 substrates were cleaned in TCE (trichloloethylene), were heated to 440 °C; Ti ion cleaning continued for 10 min. During deposition, working pressure was maintained at 0.97 Pa. Table 1 shows processing parameters in detail.

The crystal structure of the TiN coating was confirmed by X-Ray Diffraction, and TiN thickness was measured by Scanning Electron Microscope in a cross-sectional view. The elastic modulus and hardness of TiN coating were estimated by nano indentation (Triboscope, Hysitron Inc., MN, USA). Load was applied from 1 to 10 mN for 20 data points, and then the average hardness and elastic modulus were calculated. Adhesion strength of TiN on Si_3N_4 was measured by a scratch tester (CSEM, CSEM Inc., Swiss). A diamond cone with a 200 μm tip radius was used for scratch test at a loading rate of 100 N/min and a scratch speed of 10 mm/min. Adhesion strength, L_c,