Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Thin Solid Films 500 (2006) 190 – 196
thin solid films
www.elsevier.com/locate/tsf

Effect of substrate rotation on structure, hardness and adhesion of magnetron sputtered TiB_2 coating on high speed steel

N. Panich *, Y. Sun

School of Materials Science and Engineering, Nanyang Technological University, Nanyang Avenue, 639798 Singapore

Received 3 February 2005; received in revised form 31 August 2005; accepted 21 November 2005
Available online 28 December 2005

Abstract

Titanium diboride (TiB_2) coatings have been deposited on stationary and rotating high speed steel substrates by magnetron sputtering of a TiB_2 target. The structure and hardness of the coatings and the coating–substrate adhesion have been investigated by X-ray diffraction, field emission scanning electron microscopy, nanoindentation and microscratch tests. The results show that substrate rotation has a significant effect on these structural and properties features. It was found that, with substrate rotation, the TiB_2 coating exhibits a columnar structure with random orientation and relatively low hardness and coating–substrate adhesion. On the other hand, without substrate rotation, the TiB_2 coating shows a strong (001) texture with dense, equiaxed grain structure. The hardness and coating–substrate adhesion of the coatings deposited on stationary substrates are much higher than those deposited on rotating substrates. The observed phenomena are discussed in terms of the energy of the sputtered flux, which varies with the substrate–target distance during deposition.

PACS: 68.55.−a
Keywords: Adhesion; Hardness; Sputtering; Borides

1. Introduction

Titanium diboride, TiB_2, is a ceramic compound with a hexagonal crystal structure and possessing many interesting physical, mechanical and chemical properties, such as high hardness, good chemical stability and good thermal and electrical conductivity. There have been increasing interests in fabrication of this material in thin film and coating forms for many potential applications, for example to reduce wear and corrosion in engineering components and particularly in material processing tools and dies [1–5]. Among the many coating deposition techniques employed so far, non-reactive sputtering from a TiB_2 target is the most widely used for TiB_2 coating fabrication [4–7]. Although the structures and properties of sputter-deposited TiB_2 coatings have been studied by many investigators in recent years [1,3,6,8], the commercialization of sputtered TiB_2 coatings has been hindered mainly due to the difficulties in producing high quality coatings with good mechanical properties suitable for industrial applications.

Several problems exist in the production of high quality TiB_2 coatings by sputtering. First, the reported hardness of TiB_2 coatings varies widely, from 20 GPa to 70 GPa [5,6]. There are sufficient evidences to suggest that the hardness of TiB_2 coatings is determined by the crystallite size, coating density and more importantly coating texture, which are affected by deposition conditions. It is known that TiB_2 coatings with the basal plane (001) parallel to the surface exhibits the highest hardness compared to TiB_2 coatings with other orientations [9]. The second problem lies in the high residual stresses evolved in the sputtered coating, which deteriorate the mechanical integrity of the coating–substrate system [1]. Such a problem has recently been tackled by Berger et al. [7] by applying a positive bias during sputter deposition of TiB_2 coatings. A further major problem is that TiB_2 coatings are very brittle and usually have poor adhesion with metallic substrates, which is the main barrier for the industrial application of TiB_2 coatings. Recently, several attempts have been made to overcome these problems, for example by sputter cleaning the substrate [12], applying substrate bias during

* Corresponding author. Fax: +65 6790 9081.
E-mail address: panich@pmail.ntu.edu.sg (N. Panich).

0040-6090/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2005.11.055

deposition [7,10], annealing after deposition [3,4], forming multilayer and composite coatings [11–13] and introducing nitrogen during deposition [14,15].

During sputter deposition, it is a common practice that the substrates on the working table are rotating around its normal in order to achieve uniform deposition over the substrate surfaces to be coated. It is thus obvious that, with substrate rotation, the substrate–target distance is not a constant but varies from the shortest to the longest within one cycle of rotation. Substrate–target distance is known to affect not only the deposition rate, but also the energy of the adatoms arriving the substrate surface [16]. Therefore, the structure and properties of the coatings are expected to be influenced by substrate rotation. Indeed, a recent study on electron beam physical vapour deposition of ZrO_2 based coatings by Wada et al. [17] showed that substrate rotation has a strong effect on the structural development of the coating, in terms of morphology, grain structure and coating texture. However, very few detailed studies have been conducted to investigate the effect of substrate rotation on the structures and properties of sputter deposited coatings, in particular TiB_2 coatings [18].

The purpose of this work is to study the effect of substrate rotation on the structures and properties of sputter-deposited TiB_2 coatings. For this purpose, TiB_2 coatings were deposited onto stationary and rotating high speed steel substrates, and the structures and properties of the coatings were characterized by several analytical and experimental techniques. This paper reports and discusses the results obtained in this work.

2. Experiment details

High speed steel (HSS) was chosen as substrates in this study. The commercial HSS, SECO WKE45 (Sweden) in fully hardened and tempered condition was cut into $12 \times 12 \times 3$ mm^3 pieces. The specimen's surface was manually ground and polished. The HSS substrates were then ultrasonically cleaned with acetone and ethanol before charging the deposition chamber. High-purity argon gas was then introduced into the chamber after it was evacuated to below 5×10^{-4} Pa. The targets, i.e. TiB_2 and Ti, which were 75 mm diameter and 5 mm thickness, were located above the 200 mm diameter working table with an inclined angle of 30° with respect to the normal of the working table. The TiB_2 target was powered in the radio frequency (rf) mode and the Ti target was powered in the direct current (dc) mode. The substrates were positioned near to the edge of the working table below the TiB_2 target (see Fig. 1). The shortest distance between the TiB_2 target and the substrate was 60 mm. Thus, as the table rotated, the substrate–target distance varied from 60 mm to about 210 mm within one cycle of substrate rotation. All the experiments were conducted at a constant working pressure of 0.65 Pa, a total gas flow rate (Ar) of 20 sccm, a constant substrate temperature of 400 °C and a constant rf sputtering power (for TiB_2 target) of 200 W. A thin (about 50 nm) pure Ti interlayer was deposited first in all cases, by sputtering the Ti target for 10 min with a dc power of 200 W. No sputter-cleaning of the substrate before deposition and no substrate biasing during deposition were used. Two sets of depositions were conducted for various times, one with the working table rotating at 2 rpm and the other without rotation of the working table, i.e. the substrates were stationary and the substrate–target distance was kept constant at 60 mm.

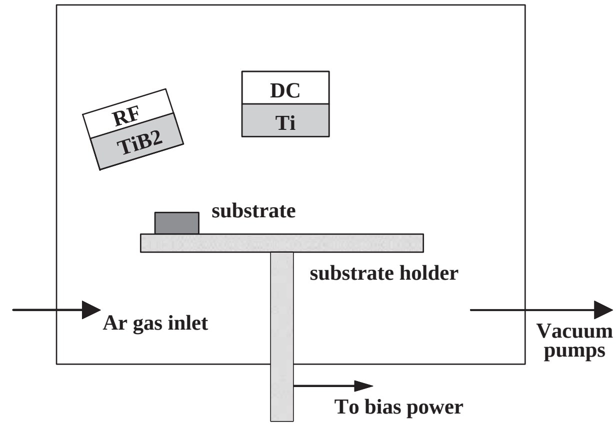

Fig. 1. The deposition set up in this study. The substrate holder was either stationary or rotating at 2 rpm.

The phase composition of the resultant coatings was examined by Rigagu X-ray diffractometer with Cu-Kα radiation. Crystallographic phases were deduced by comparing the experimental diffraction patterns with the Joint Committee for Powder Diffraction Standard data [19]. The morphology of surfaces and fractured cross-sections of the coatings were imaged using a field emission scanning electron microscope (FESEM), Jeol JSM 6340F. The coating thickness was measured by making a ball-crater on the coating surface using the Calotest machine manufactured by CSEM. A stainless steel ball of 25.4 mm diameter was used for cratering with a speed of 500 rpm for 240 s.

Nanoindentation test was performed using the NanoTest™ instrument (Micro Materials Limited, UK), with a Berkovich diamond indenter. All experiments were performed at a constant loading and unloading rate of 0.05 mN/s and to a penetration depth of 50 nm. The unloading curves were used to derive the hardness and reduced modulus values by the analytical technique developed by Oliver and Pharr [20]. The reported hardness and modulus values are the average of 10 measurements.

The microscratch test was performed using the multipass microscratch mode available in the NanoTest™ device with a diamond indenter topped with a conical with spherical end form of 25 μm in radius. A new test method was employed in this work, as described by Xia et al. [21] and detailed below with reference to Fig. 2.

For each test, a set of surface profiles along the track was measured. Firstly, the initial track profile before scratch (BS profile in Fig. 2) was measured by scanning across the full length of distance to be scratched with a small load of 0.25 mN. Then, the scanned length was scratched by applying a linearly increasing load at 5 mN/s after pre-scanning the initial 300 μm distance under a small initial load of 0.25 mN (from A to B in Fig. 2). During scratching, the friction force on the indenter and the surface profile along the full length of the scratched track were measured continually, such that a friction force versus