MICROSTRUCTURE AND TRIBOLOGY OF TiB_2 AND TiB_2-TIN DOUBLE-LAYER COATINGS

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Abstract

TiB_2-TiN double-layer coatings have been prepared by ion beam enhanced deposition. AES, XRD, TEM and HRTEM were employed to characterize the TiB_2 layer. The microhardness of the coatings was evaluated by an ultra low-load microhardness indenter system, and the tribological behavior was examined by a ball-on-disc tribology wear tester. It was found that in a single titanium diboride layer, the composition is uniform along the depth of the film, and it is mainly composed of nanocrystalline TiB_2 with hexagonal structure, which resulted from the ion bombardment during the film growth. The hardness of the TiB_2 films increases with increasing ion energy, and approaches a maximum value of 39 Gpa at ion energy of 85 keV. The tribological property of the TiB_2 films is also improved by higher energy ion beam bombardment. There is no major disparity in the mechanical properties of double-layer TiB_2/TiN coatings and TiN/TiB_2 coatings. Both show an improved wear resistance compared with single-layer TiB_2 films. The adhesion of double-layer coatings is also superior to that of single-layer films.

1. Introduction

For bulk metallic materials, it is known that maximum wear resistance is obtained at a specific favorable combination of hardness and toughness [1]. With hard ceramic material coatings, a similar behavior should be expected. The main problem in optimizing hard coatings therefore seems to be increasing the toughness while maintaining high hardness. But generally it is an exacting requirement for single-layer coatings. Titanium diboride is the hardest metallic materials with Vicker's hardness of 3000 kg/mm^2 [2]. However, it is brittle compared with other metallic materials, such as TiN and CrN. Thus, a design of combination of double-layer coatings, employing hard TiB_2 and tough TiN, was motivated. The present paper reports the investigation on microstructure of single-layer TiB_2 films and then the study of tribological behavior of the films, and its combination with TiN films. Both TiB_2 and TiN films were prepared by ion beam enhanced deposition (IBED).

2. Experimental details

In this study, the preparation of titanium diboride and titanium nitride films were conducted on an EATON Z-200 ion beam mixing system. The details of the system was described elsewhere [3]. For deposition of titanium diboride films, high purity sintered titanium diboride and xenon gas were used as source materials for electron beam evaporation and ion bombardment respectively. The evaporation rate was 6 A/sec, the ion beam current density was 32 $\mu A/cm^2$. The ion energy varied from 25 keV to 85 keV. The pressure in the processing chamber was 5×10^{-3} Torr as base, and reached a magnitude of 6.7×10^{-6} Torr during processing because of leakage of xenon gas from the ion source. The temperature of samples was ambient during the growth of the film on a water-cooling substrate holder. Mirror-polished semiconductor-grade silicon wafers and SKD11 steel were selected as substrate. The thickness of this single-layer is 1 μm.

The experimental parameters for synthesis of TiN films has been previously reported by the co-authors [4]. Two types of double-layer coatings have been prepared with ion energy of 40 keV. The first type is named as TiN/TiB_2. A TiB_2 layer was first deposited on the silicon substrate, then a TiN layer was deposited on the top of the as-deposited TiB_2 film. The second is named as TiB_2/TiN, where the TiB_2 film is on the top, and TiN lies between the TiB_2 film and substrate. The thickness of each sub-layer in the double-layer coatings is 0.5 μm.

The formed films were characterized by Auger electron spectroscopy (AES), X-ray diffraction (XRD), transmission electron spectroscopy (TEM) and high resolution transmission electron spectroscopy (HRTEM). The adhesion of film to substrate was measured by a scratch tester. The plastic and elastic deformation was investigated using an ultra low-load microhardness indenter system, which measures the depth of penetration of the indenter as a function of the applied force. The displacement of the indenter is measured with a resolution of 1 nm, while the resolution of the load system is 0.01 mN.

The tribological behavior of the formed films was evaluated using a tribology wear tester. The ball-on-disc tribology wear tester, of which a sample was fixed at the center, rotated horizontally sliding velocity of 0.2 m/s. Wear tests for all samples were carried out under dry running conditions against Al_2O_3 ceramic balls in laboratory air. The hardness of the ceramic ball is 1800 Hv, and the diameter is 0.1 mm. During the wear test, the humidity was 30~35% at room temperature. The wear tracks and friction coefficient were then studied for characterizing the tribological properties of the films.

3. Results and discussion

3.1 Single-layer TiB_2 film

AES analysis showed that all components distribute evenly over the whole film. It was found that the boron-to-titanium ratio is 2.1, a little higher than the stoichiometrical composition.

It was revealed by XRD and TEM studies that the formed film is mainly composed of TiB_2 phase with hexagonal structure. Figure 1a is the electron diffraction pattern of an IBED TiB_2 film, in which three rings could be seen. These rings correspond (100), (101) and (110) diffraction peaks of hexagonal TiB_2. In order to understand the mechanism of crystallization of TiB_2 at ambient temperature, the microstructure of a simple e-beam evaporated film was also investigated, as shown in fig. 1b. The diffuse rings indicate that the film is amorphous without ion bombardment. It implies that ion bombardment could greatly enhance the crystallization of film grown at ambient temperature.

For further study of the microstructure of the film, HRTEM was employed to directly observe the film. It was found that even though the component ratio is a constant along the depth of the film, the microstructure along the film depth is different. The upper part of the film is composed of TiB_2 nanocrystallites with average size of several nanometers, while the lower part close to the substrate is complete amorphous, as shown in fig. 2a and 2b.

Figure 3a and 3b are SEM micrographs of scratch tracks on an e-beam evaporated TiB_2 film and an IBED TiB_2 film. The scratch track of the IBED film is smooth and narrow. However, the film without ion bombardment is seriously cracked. These demonstrate the IBED could improve the adhesion between film and substrate significantly. The strong adhesion is of great importance to the practical application.

Hardness is the reflection of plastic property of material. For a complete study of deformation of a material, evaluation of elastic behavior of material is also needed. Yang's modulus is one of the important parameters characterizing material elastic property. With the UMIS-2000 ultra low-load microhardness indenter system, which was developed at CSIRO Division of Applied Physics, Australia, the microhardness and Yang's modulus could be obtained in a single loading and unloading run. Figure 4 shows the hardness and Yang's modulus versus the ion energy. The maximum load for hardness test is 2g. It could be seen that the hardness and Yang's Modulus increase with increasing the ion energy. The maximum hardness achieved at ion energy of 85 keV is 39 Gpa, equivalent to 3600 kgf/mm^2, higher than the bulk TiB_2. It was believed that the nanocrystallite is responsible for the high hardness.

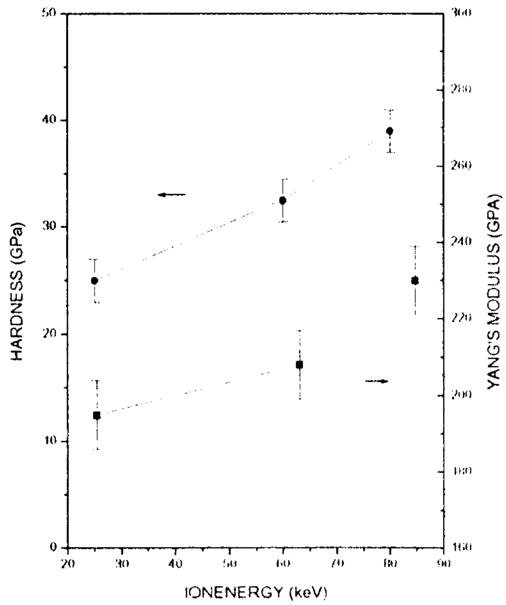

Figure 4 The microhardness and Yang's Modulus versus the ion energy

SEM micrographs of wear tracks of the films prepared with different ion energy are presented in fig. 5a, 5b and 5c. The applied load in the wear test is 0.02kgf. The micrographs show the different wear behaviors for the different films. The wear track of the film prepared under 25 keV ion bombardment exhibits a considerably wide and pronounced irregular concave up to a depth of 0.8 μm, which was measured by a surface rough sketching apparatus. In contrast, for films prepared under 60~85 keV ion bombardment, the wear tracks are narrow and considerably smooth with depth of approximately 0.1 μm. From the coefficient of friction, the relation between ion energy and film tribology could be examined further. Figure 6 shows the friction coefficient versus sliding time for the samples corresponding the wear tracks in fig. 5a, 5b and 5c. It could be seen that the friction coefficient of the film prepared with 25 keV ion bombardment increases rapidly at the initial stage of the wear test, while the friction coefficient of the films prepared under 85 keV ion bombardment keeps a low value for a period of 400 seconds. The above results suggest that high energy ion beam assistance may improve the tribological behavior of IBED films at the present studied ion energy range.

3.2 Double-layer TiB_2 - TiN coatings

For a complete understanding of double-layer coatings, we have changed the order of sub-layers in the double-layer coatings. Both TiB2/TiN and TiN/TiB2 coatings have been prepared by IBED. We examined the adhesion of both types of double-layer coatings. Scratch tests indicated that the critical load, which reflects the adhesion of film to substrate, for both double-layer coatings is 4.3 kg, higher than that of single-layer TiB_2 film, 2.8 kg. This implies that the adhesion could be improved by double-layer structure. The possible explanation is that the crystal structure of TiB_2 match very well with the structure of TiN on the (001) plane of TiB_2 and (111) plane of TiN. The atomic distance between Ti atom on the (111) plane of TiN is 0.300 nm, and the atomic distance between Ti atoms on the (001) plane of TiB_2 is 0.303nm.

The TiB_2 -TiN double-layer coatings were designed to improve the tribology of the coatings. Figure 7 is the friction curves, showing the measured friction coefficient versus the sliding time, for single-layer TiB_2 film and double-layer TiB_2-TiN coatings. The applied load is 0.1kgf. It could be seen that the friction coefficient of single-layer TiB_2 film changes abruptly at the beginning of the wear to a high friction coefficient of 0.8. In contrast, the both double-layer coatings keep a low friction coefficient for a considerably long time. This implies that the wear resistance was increased by double-layer coatings.

4. Conclusion

TiB_2-TiN double-layer coatings have been prepared by ion beam enhanced deposition. The microstructure study showed that the TiB_2 layer is mainly composed of nanocrystalline TiB_2 phase with hexagonal structure, however, the part close to the substrate is amorphous. By increasing ion energy, TiB_2 films with better mechanical properties could be achieved. Double-layer coatings of TiB_2-TiN could improve the tribological behavior of the surface coatings.

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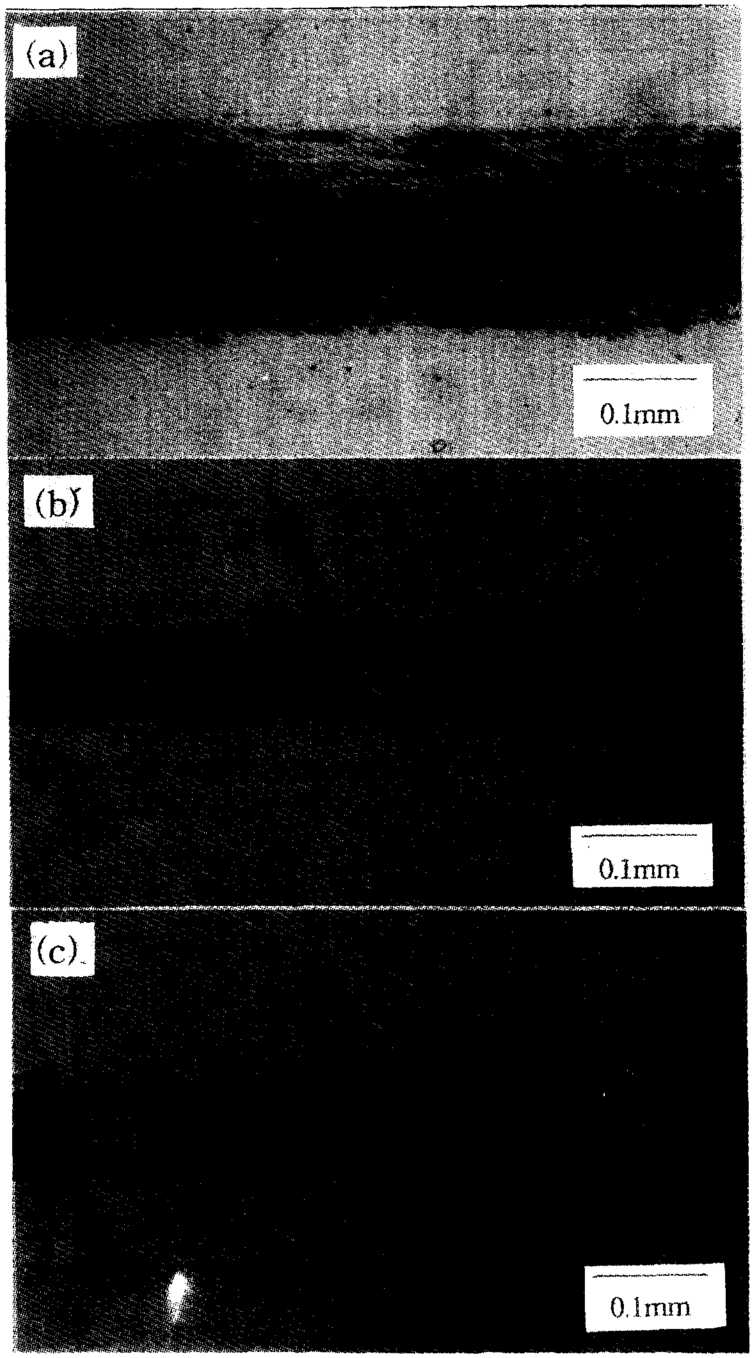

Figure 5 SEM micrographs of wear tracks of TiB_2 films prepared with ion energy of (a) 25 keV, (b) 60 keV and (c) 85 keV

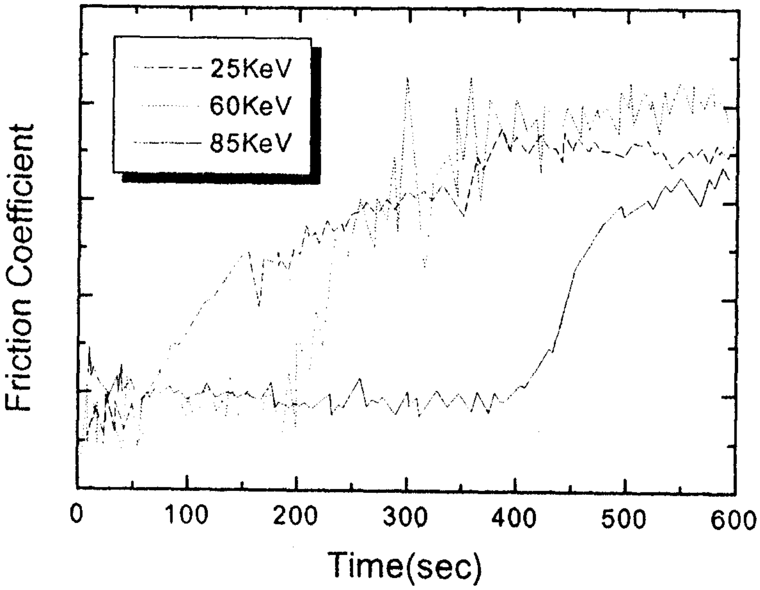

Figure 6 The friction coefficient versus sliding time for TiB_2 films under 25 keV, 60 keV and 85 keV ion bombardment

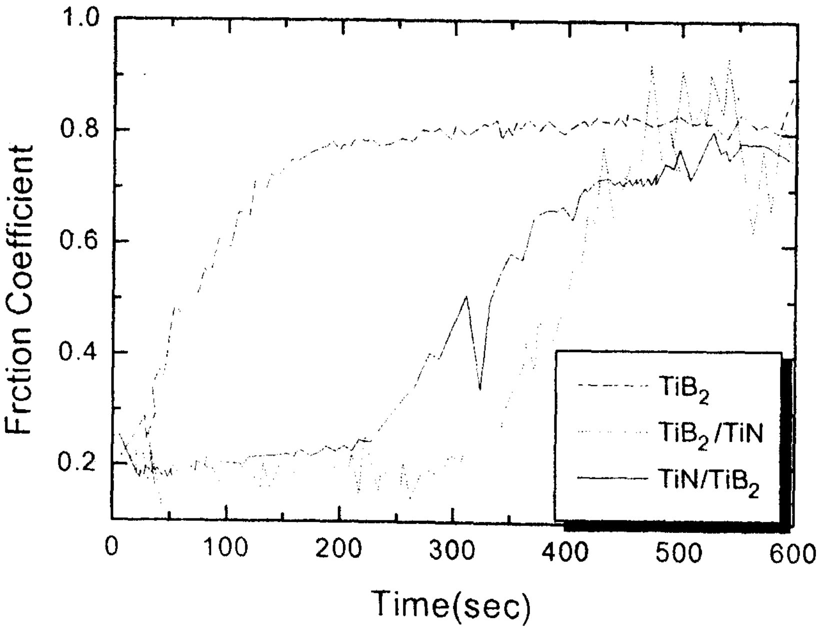

Figure 7 The friction coefficient versus sliding time for single-layer TiB_2 film, TiB_2/TiN and TiN/TiB_2 double-layer coatings