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Mechanical and tribological properties of a-C/a-C:Ti multilayer films with various bilayer periods

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ABSTRACT

Thick a-C/a-C:Ti multilayer films with bilayer periods of 12–70 nm were deposited on Ti6Al4V alloy substrate by means of closed field unbalance magnetron sputtering. The morphology and microstructure of the multilayer films were investigated by scanning electron microscopy, high resolution transmission electron microscopy and X-ray photoelectron spectroscopy. Nanocrystalline TiC was distributed in the a-C:Ti layer and at the interface between the two adjacent layers. The mechanical and tribological properties were evaluated by Rockwell and scratch tests, a nanoindentor and a ball-on-disk tribometer. The multilayer film with a bilayer period of 12 nm showed the highest adhesion strength, hardness (26 GPa) and elastic modulus (232 GPa); it also had the lowest average coefficient of friction (0.09) and a wear rate of 8.06×10^{-17} m^3 N^{-1} m^{-1}.

1. Introduction

Amorphous carbon (a-C) thin film is an important material for biomedical and tribological engineering applications because it possesses good biocompatibility, superior wear resistance, high hardness and low coefficient of friction [1–3]. However, the high internal stresses originating growth prevent the deposition of thick films, and its high hardness makes it difficult for the a-C layer to comply with metal substrate deformation, which can lead to massive failure of the film and restrain its practical application [4]. Some efforts have been employed to minimize the residual stress and improve the adhesion of a-C films by depositing an interlayer or transition layer between the films and the substrate [5–8]. The multilayer structure is another effective approach by uniformly embedding layers with different components into a-C films. Because the interfaces and possible grain boundaries in the multilayer structure of the films can deflect and reduce crack propagation, restrain the growth of grain size and reduce the stress concentration, consequently it can improve the mechanical properties and wear resistance [9–11]. Many studies have been performed by choosing transition metal (such as Ti, Cr, Ag and W) as embedding layers, forming metal/a-C multilayer films [12–14]. Such films show improved adhesive strength but their low hardness always cannot meet their practical applications. Nanocomposite films comprising of nanocrystalline grains in an amorphous matrix have excellent mechanical and tribological properties [5,15–20]. Compared with the metal layer, the composite layer consisted of metallic element doped into the a-C matrix may show good toughness and high hardness. For the biomedical applications such as replacement of the hip joint, Ti element is an excellent choice because of its enhanced biocompatibility.

As mentioned in Stueber et al. [21], interfaces in the multilayer can have a beneficial effect on the properties of the film when their amount is carefully adjusted to the overall volume of the film. In other words, tailored properties can be achieved at a smaller bilayer period. For example, Chen et al. [22] reported that the TaN/a-CN_x multilayer film at a small bilayer period of 10 nm showed the best mechanical and tribological properties. While Liu et al. [23] revealed that the carbon nitride multilayer film with a larger bilayer period of 60 nm had the highest hardness and best wear resistance, which presented a different variation trend. In this present work, based on the previous work [24], different bilayer periods of a-C/a-C:Ti multilayer films were deposited by closed field unbalance magnetron sputtering. The effects of bilayer period on the mechanical and tribological properties of a-C/a-C:Ti multilayer films were further investigated.

2. Experimental

2.1. Deposition of multilayer films

The a-C/a-C:Ti multilayer films were deposited on Ti6Al4V alloy and Si (100) wafer substrates by a closed field unbalance magnetron sputtering system (TAJS-700, TENGAO). The schematic image of the vacuum chamber of closed field unbalance magnetron sputtering was shown in Fig. 1. Two titanium targets and two graphite targets (380 mm × 127 mm in sizes), located about 10 cm away from the substrates, were alternately arranged in the chamber. The films deposited

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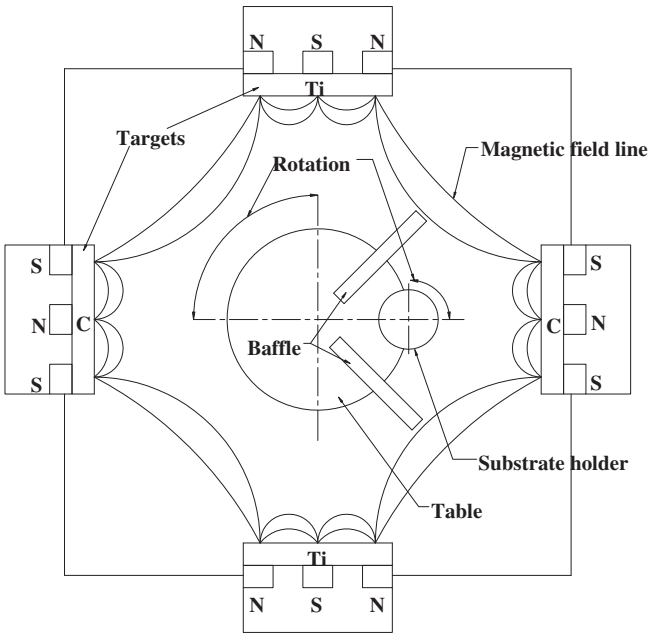

Fig. 1. Schematic image of the vacuum chamber of closed field unbalance magnetron sputtering.

on the silicon wafers were only used to characterize their microstructure and chemical composition. All the substrates were ultrasonically cleaned in acetone for 20 min, in ethanol for 10 min, and then blow-dried by nitrogen, to clear impurities on the surface. Prior to deposition, the base pressure of the sputtering system was evacuated to 4×10^{-3} Pa, and then argon gas was introduced to keep the process pressure of 0.2 Pa. The substrates were etched by Ar^{+} bombardment at a negative bias of 500 V for 30 min, in order to remove the oxides and adsorptions. Then a thin Ti buffer layer was deposited onto the substrates for 10 min, with a negative bias of 200 V. The rotation speed of the substrate holder was kept at 5 rpm and then a carbon: the Ti transition layer with a gradient content ratio of Ti/C was deposited by gradually decreasing the titanium target current from 3 A to 1 A, and increasing the graphite target current from 0 to 3 A for 60 min. Subsequently, the multilayer films composed of thin sequential carbon layer and carbon-Ti composite layer were deposited by alternately shutting out the titanium target. And the top layers of all the films are a-C layers. During the deposition, the current of the graphite and titanium targets was kept at 3 A and 1 A, respectively, with a negative bias of 100 V. The bilayer period was controlled by the sputtering time over the Ti and C targets. Through the above deposition process, a series of a-C/a-C:Ti multilayer films were designated as M1, M2, M3 and M4 with different bilayer periods, respectively 70 nm, 53 nm, 35 nm and 12 nm. The detailed parameters for the deposition of the graded layer are summarized in Table 1. In this present work, the total thicknesses of multilayer films were about 2.8–3.0 μm.

2.2. Characterization of films

The surface and cross-section morphologies of the multilayer film were characterized by a scanning electron microscope (SEM, Hitachi S-4800 equipped with GENENIS 4000 EDAX detector). The microstructure observation was carried out with a transmission electron microscopy (TEM, Tecnai G2F30 S-Twin). The cross-section samples were prepared by mechanical polishing and Ar ion-milling (Gatan 691). The bonded structures of films were characterized by an X-ray photoelectron spectroscopy (XPS) using an ESCALab 220i-XL electron spectrometer, operating with a monochromated Al-Kα X-ray radiation source in a base pressure of 10^{-7} Pa. The binding energies were referenced to the C 1s line at 284.6 eV from adventitious carbon.

The hardness and Young's modulus of the films were obtained using a nanoindentor (Agilent technologies, G-200) with a Berkovich diamond indenter and the theory developed by Oliver and Pharr. The maximum indentation depth was kept around 10% of the film thickness to minimize substrate effects. 6 indentations in each sample configured on different areas were performed to have reliable statistics.

Adhesion tests were performed on the films through the scratch and Rockwell tests. Standard scratch tests were used to assess the transverse adhesion with a conventional scratch tester (WS-2002 equipped with an acoustic emission detector). For these scratch tests, a diamond pin (0.2 mm in radius) was drawn across the surface of the film at a constant linear velocity of 4 mm min^{-1}, while increasing the load linearly from 0 to 80 N. Standard Rockwell tests were performed using a Rockwell hardness tester (HR-150A, Xinnuo Testing Instrument Co.) at a load of 100 kg using a Rockwell indenter of 0.2 mm in diameter to assess the vertical adhesion of the films. The scratch and Rockwell craters were observed by an optical microscope (Nikon Eclipse ME600D).

The tribological properties of the multilayer films were performed on a WTM-1E ball-on-disk tribometer at room temperature. Si_3N_4 ceramic ball (4 mm in diameter, hardness HV = 1550) was used as the counter body. The tests were carried out at a normal load of 10 N at a sliding velocity of 0.2 m s^{-1} in ambient air (50% RH). The coefficient of friction was monitored continuously during the tests by a linear variable displacement transducer and recorded on a data acquisition computer attached to the tribometer. Test duration was up to 60 min. The wear rates of the films were calculated from measuring the traces of surface profiles taken across the wear track using a Dektak 3 contact profilometer.

3. Results and discussion

3.1. Microstructure of multilayer films

Fig. 2 shows the cross-sectional SEM morphologies of a-C/a-C:Ti multilayer films with different bilayer periods. As seen in Fig. 2a, c, e and g, the thicknesses of all the films are about 3 μm. To some extent, the cross sectional morphology reflects the growth mode of the film, which exhibits the columnar characterization perpendicular to the substrate. The corresponding surface morphologies of the insets in Fig. 2 present masses of well defined uniform clusters constituting dense surfaces, due to high energetic ion bombardment effect by magnetron

Table 1
Depositing parameters for graded layer of a-C/a-C:Ti multilayer films.

Process	Substrate cleaning	Target cleaning	Underlayer	Transition layer
Time (min)	20	5	10	60
Substrate bias (V)	−500	−500	−200	−100
Ti target current (A)	0.2	0.2	3	3 → 1
C target current (A)	0	0.2	0.2	0.2 → 3
Degree of vacuum (Pa)			0.2	