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Tribological performances of the graphite-like carbon films deposited with different target powers in ambient air and distilled water

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ABSTRACT

Graphite-like carbon (GLC) films were deposited using magnetron sputtering technique with different target currents. With the increase of target current, the deposition rate and sp^2 site increased, while the mechanical properties and film compactness decreased. In ambient air, decreased elastic modulus led to the high friction of GLC film. In distilled water, water lubrication resulted in the similar low friction coefficients if the GLC film could survive. The decrease of mechanical properties caused the increase of specific wear rate in ambient air. The decrease of film compactness generated the increase of specific wear rate in distilled water.

1. Introduction

The graphite-like carbon (GLC) film, which characterized the amorphous carbon with significant sp^2-hybridized carbon sites (graphite-like microstructure), has attracted great scientific interest due to the special microstructure comparing with the other carbonaceous materials as well as the beneficial properties including high hardness and favorable self-adapted tribological properties in different environments, recently [1–4]. Baptista et al. formed the sp^2-rich amorphous carbon structure with high hardness of approximately 14 GPa by ion beam irradiation of fullerene, a-C and polymeric a-C:H films [2]. The authors argued that the distortion in the sp^2 bond angle gave rise to the formation of non-six-membered rings that allow curvature and the formation of a cross-linked three-dimensional network, therefore, the strong sp^2 σ-bonded three-dimensional carbon structure provided a rigidity network with high hardness. Lacerda et al. prepared the hard GLC films with high stress and local microscopic density using the IBAD technique [3]. They proposed that the reduction of interplanar distance and the random distribution of sp^2 cluster crosslinked by a small concentration of sp^3 sites could form hard carbon matrix with a pronounced graphite-like characteristic. Field et al. fabricated the GLC film with almost entirely sp^2 bond using magnetron sputtering technique, and reported the sputtering GLC film was generally dense and amorphous carbon including fine regions of nano-crystalline graphite within the matrix [4].

Different to most of the other amorphous carbon films, the sputtering GLC showed low environmental sensitivity. For example, the hydrogenated amorphous carbon (a-C:H) film would show the increased friction and wear in humid circumstance though it could exhibit low friction and wear in vacuum [5]. Ronkainen et al. even found the early failure of the a-C:H film in water-lubricated condition [6]. However, the sputtering GLC could show low friction and wear in either the ambient air or water environment [7]. Moreover, Wang et al. found that the friction and wear of the sputtering GLC film would decrease further in distilled water comparing with that in ambient air [8]. This self-adapted low friction and wear performances in either ambient air or water environment of GLC film were significant to water lubrication systems, which were considered as the substitutes for traditional oil lubrication systems in modern industry [9–11]. The benefits for water lubrication included environmental compatibility, energy efficient and user friendly [12,13]. But the lubricating effect of water was poor due to its low viscosity. So that high friction or severe wear of the water-lubricating components would take place when solid–solid contact occurred during starting and stopping, running-in and occasional overload [14,15]. The high performance sputtering GLC film with low friction and wear in both ambient air and water environment might be one of the best approaches to this problem i.e. ensuring the low friction and wear of the friction contact surface even if there was a lack of lubrication.

Generally, the microstructure and properties of the amorphous carbon film were highly dependent on the depositing conditions. Wang et al. found that the sputtering GLC film wear out quickly in water if there was a loose microstructure formation under low bias voltage [16]. Therefore, the effects of different deposition

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conditions on the tribolgical performances of GLC film in ambient air and water should be widely studied. In this paper, we deposited the GLC film using magnetron sputtering technique with different target currents. The microstructure and properties of GLC film as the function of the target current were investigated systematically. The main object was to study effects of the target power on microstructures and tribological performances in two environments of ambient air and water of the GLC film.

2. Experimental details

2.1. Film preparation

The GLC films were fabricated on Si(1 0 0) wafers for microscopic observations and stainless steel (18Cr–12Ni–2.5Mo) substrates for mechanical and tribological tests by magnetron sputtering deposition technique in Ar atmosphere. The depositing system was configured of three magnetron target positions which focused on a sample seat. High pure graphite target was fixed in the middle target positions, and two twinborn Cr targets were fixed on the other two target positions. Purities of graphite and Cr targets were 99.95% and 99.8%, respectively. All the targets had the same dimensions of 6 mm × 76 mm × 173 mm. The middle magnetron with graphite target was supplied by a DC power. The other two magnetrons with Cr targets were supplied by a mid-frequency (40 KHz) AC power. The sample seat was connected with a pulse-DC power (40 KHz). Vacuum pressure in the chamber was pumped and controlled by a turbo molecular pumping system.

Prior to deposition, the substrates were cleaned ultrasonically in ethanol and acetone baths in succession and dried with a blower. Then the substrates were fixed on the sample seat in the vacuum chamber. When the base pressure of the vacuum chamber reached to 1.0×10^{-3} Pa, Ar gas with a constant flow 100 sccm was introduced to the chamber and the vacuum pressure was adjusted to 1.0 Pa by a throttle. After that, the substrates were DC sputter-cleaned for 15 min at bias voltage −1000 V (duty cycle 50%). Then Cr interlayers were firstly deposited on the substrate surfaces for 15 min to improve the adhesion between substrates and GLC films [17,18]. Current of the twinborn Cr targets was 2.0 A, and bias voltage on substrates was −500 V (duty cycle 50%). On top of the Cr interlayers, GLC layers were deposited for 100 min with different graphite target currents ranged from 0.4 to 2.0 A. The DC power connected with the graphite target worked under the constant current mode. Target voltage would self-adjust due to the target current. Since the surface area of target could be determined, the power densities of graphite targets at different currents were calculated which are shown in Table 1. The bias voltage for each deposition of GLC layer was −300 V (duty cycle 50%).

2.2. Film characterizations

Raman spectra in the range of 800–2000 cm^{-1} of GLC films were acquired by an inVia-reflex Raman spectrometer using an Ar^+ laser of 532 nm with a resolution of 1 cm^{-1}. The laser power density was lower than 1 mW mm^{-2} to avoid the possible beam-induced graphitization. X-ray photoelectron spectroscopy (XPS) measurements were carried out using an AXIS Ultra DLD spectrometer. C1s spectra were collected using a monochromatic AlKα (1486.6 eV) X-ray source operated at 150 W, and at a pass energy of 10 eV. In order to liberate the surface from adventitious contamination, each sample was cleaned by Ar^+ at a beam voltage of 2 kV, and sputter area of 2 mm × 2 mm. The sputtering time was 1 min. Surface and cross sectional morphologies of GLC films were investigated using S-4800 scanning electron microscope (SEM).

After measuring the bending of coated substrate with a surface profilometer, the film internal stress was calculated by Stoney's equation [19]. Mechanical properties including hardness and elastic modulus were measured by a NANO G200 nanoindenter apparatus with a Berkovich indenter at a load of 50 mN. The maximum indenting depth was approximately 10% of the film thickness [20]. The tribological performances of GLC films were tested by a UMT tribo-meter under reciprocating mode in both ambient air and distilled water at room temperature. The relative humidity of the circumstance was approximately 40%. The distilled water was exerted onto the sample by dropper. WC balls with a diameter of 3 mm were used as the counterparts. All frictional tests were performed under a load of 2 N with the amplitude of 5 mm and the frequency of 5 Hz. The maximum contact pressure calculated from the Hertz model for a ball on a flat surface was approximately 1.5 GPa. Each tribo-test was performed 4000 s.The statistic friction coefficient and specific wear rate of each film were obtained by averaged four tests. The specific wear rate was calculated using the equation [21]: $K=V/SF$, where V is the wear volume in m^3, S is the total sliding distance in meters and F is the normal load in newtons. Wear volume V was determined by integrating the cross-sectional profile of the wear track which was profiled by a contact surface profiler. The friction contact surfaces of WC balls were also analyzed by SEM and Raman spectrometer.

Table 1
Power densities of the graphite target at different currents.

Target current (A)	Target voltage (V)	Target power (W)	Target power density (W/mm^2)
0.4	420	168	0.013
0.8	650	520	0.040
1.2	740	888	0.068
1.6	770	1232	0.087
2.0	790	1580	0.120

3. Results

3.1. Microstructures of GLC films

The cross-sectional and surface morphologies of GLC films deposited with different target currents are shown in Fig. 1. The left pictures in Fig. 1 are cross-sectional morphologies. It can be seen that the thickness of GLC layer increases gradually with the increase of target current. The cross-sectional morphology of GLC film deposited with low target current illustrates the uniform and compact microstructure, while, the GLC film deposited with high target current shows loose microstructure with columnar morphologies. The right pictures in Fig. 1 are surface morphologies of GLC films. When the target current is low, the surface of GLC film reveals a kind of dual structure that is the fine grains aggregated into packs. With the increase of target current, the fine grains are coarsening, gradually, and the interfaces of bulky pack structures are disappearing. As the target current increase to 2.0 A, the surface morphology of the GLC film is mainly distributed by big grains without any packs.

Raman spectra of GLC films deposited with different target currents are shown in Fig. 2. Owing to the high sensitivity to π bonds, the conventional Raman spectrum of disorder carbon is dominated by a G peak around 1550 cm^{-1} and a D peak at about 1350 cm^{-1} [1]. Both of the G and D peaks are attributed to sp^2-bonded carbon, but the G peak is due to the bond stretching vibration of all pair of sp^2 atoms in both rings and chains, while the D mode is the breathing mode of those sp^2 sites only in rings