Diamond & Related Materials 52 (2015) 38–42

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Friction at single-asperity contacts between hydrogen-free diamond-like carbon thin film surfaces

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ARTICLE INFO

Article history:
Received 3 June 2014
Received in revised form 17 December 2014
Accepted 18 December 2014
Available online 24 December 2014

Keywords:
Nanoscale friction
Hydrogen-free diamond-like carbon
Friction force microscopy

ABSTRACT

This work investigates the friction and adhesive forces at the single-asperity contact between hydrogen-free diamond-like carbon (DLC) coated surfaces in humid air and in argon. High power impulse magnetron sputtering deposition has been used to produce hydrogen-free DLC thin films on commercial silicon AFM tips and silicon wafers. The structure and surface morphology of the deposited DLC films has been investigated by X-ray photoelectron spectroscopy and tapping AFM, investigations that showed very smooth DLC films with about 29% of sp^3 C − C bonds. The as-deposited hydrogen-free DLC thin films were hydrophilic (water contact angle about 65°) due to incorporation of a small amount of oxygen (about 9% of C = O bonds) at the film surfaces. The friction force measurements show that at low normal loading force the contact friction is much lower in the humid air than in the argon, while at large values of the loading force the contact friction does not depend on the measurement medium. A qualitative friction model based on the concept of dry and wet friction regimes, when the layer of water adsorbed on DLC film surfaces plays the role of lubricator, is proposed to explain these findings.

1. Introduction

Diamond-like carbon (DLC) coatings provide very hard, frictionally-low, chemically inert and fully biocompatible surfaces, which make them very attractive for applications in biomedicine [1] and micro electro mechanical system technology [2]. These coatings are amorphous and not as hard, dense, and optically transparent as the crystalline diamond. Their structure is a mixture between the near-planar trigonal structure of graphite, which is formed by sp^2 C − C bonds, and tetragonal structure of diamond formed by the sp^3 variety of carbon interatomic bonds [3]. The particular properties of a DLC coating are given by the ratio between sp^3 and sp^2 bond densities. A high density of sp^3 bonds assures surface hardness, but increase the brittleness and friction of coatings. On the other way, a low density of sp^3 bonds decreases the hardness and friction [4].

The frictional property of macroscopic contacts between DLC coatings has been studied by ball-on-flat tribometers [5,6], but little is known about frictional behavior of single-asperity contacts between DLC surfaces. Dunkle et al. [7] have studied the frictional behavior of a single-asperity contact between a diamond atomic force microscopy (AFM) tip and a commercially available DLC substrate in vacuum at different values of temperature. They have found a friction force proportional with the normal loading force, which is not the common dependence for single-asperity contact friction, and a slight increase of friction coefficient with the temperature. While these measurements were performed in vacuum, they give no information on the effect of moisture on the single-asperity contact friction. At macroscopic scale, it is widely recognized that the presence of water vapor in air diminishes the friction forces between many engineered surfaces including the DLC coatings [8]. The friction force in humid air at a single-asperity contact between a silicon nitride AFM tip and H:DLC coatings produced by chemical vapor deposition in methane and hydrogen plasma has been studied by Xie et al. [9]. Unfortunately, this study has not considered friction in dried atmosphere for a comparison.

The present work investigates the friction force at a single-asperity contact between hydrogen-free DLC coated surfaces. To this goal, silicon atomic force microscopy (AFM) probes and silicon wafers were covered by DLC films by high power impulse magnetron sputtering (HiPIMS) deposition in pure argon. Thus, the deposited DLC films were hydrogen-free. The hydrogen-free DLC covered AFM tips and flat samples were used in friction experiments in humid air and dry atmosphere (argon). Thus, the effect of water vapor on friction force at a single-asperity contact between hydrogen-free DLC surfaces has been evaluated. In the humid air, the friction force has a complicated nonlinear dependence on the normal loading force with an important decrease at low values of the loading force. This decrease of friction force is attributed to lubrication role of the layer of water adsorbed on the hydrogen-free DLC film surfaces. At high values of the normal loading force the

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http://dx.doi.org/10.1016/j.diamond.2014.12.007
0925-9635/

friction force was the same in dry and wet media. This is explained by exclusion of water molecules from the contact region, which determined solid–solid dry friction.

2. Materials and methods

Hydrogen-free DLC thin films were deposited on commercial silicon cantilevers (CSG 37 and NSG 35 from Mikromasch) and silicon wafers in an HiPIMS deposition chamber by sputtering pure graphite target (5 cm in diameter) in pure argon gas at a pressure of 0.7 Pa and constant flow of 16 sccm. Details on our HiPIMS experimental set up have been published elsewhere [10]. The HiPIMS discharge used voltage pulses 10 μs in width and 900 V in amplitude with a repetition frequency of 1500 Hz. In these conditions, the average discharge power was around 60 W, and the average discharge current intensity was 112 mA. The deposition substrates (silicon AFM probes and wafers) were placed at a distance of 10 cm from the graphite target. Sputtering of the carbon atoms out from the target resulted in deposition of DLC films with a growth rate of about 2.4 nm/min.

The thickness of the DLC film deposited on silicon wafers has been measured by stylus surface profilometer (Alfa Step IQ from KLA-Tencor Co.). The deposition of the DLC films on the high-aspect ratio AFM tips has been confirmed by measurements of the AFM tip radius before and after deposition. This was done by contact AFM scanning of the very sharp edges of a standard silicon grating (TGG1 from NT-MDT) with the AFM tip without (before deposition) and with a DLC coating. The topography images of the sharp edges (nominal curvature radius of 5 nm) were analyzed to extract the tip radius by deconvolution [11].

Since friction force measurements depends strongly on surface properties and the measurement medium [12], we have performed a thorough investigation of surface properties of the deposited DLC thin films. Thus, the film hydrophilicity was characterized by measurements of water contact angle values for small sessile droplets of deionized water on the DLC films deposited on silicon wafers. Then, the chemical structure of DLC thin film surface has been investigated by X-ray photoelectron spectroscopy (XPS) with PHI 5000 VersaProbe XPS system from ULVAC-PHI, Inc. The XPS spectra have been acquired by irradiating the DLC thin film surface by monochromatic Al K_α X-rays ($h\nu$ = 1486.7 eV) with the spot size of 100 μm^2. The binding energy values have been calibrated by taking the carbon C 1 s peak (284.6 eV) as reference. Curve fitting of core level C 1 s XPS spectrum with C − C sp^2, C − C sp^3 and C = O binding peaks was carried by a peak fitting software (Multi Pak 8.2 C) using the Gaussian–Lorentian function. The crystallinity of the DLC films has been investigated by X-ray diffraction (LabX XRD-6000 from Shimadzu Co.) using Cu K_α X-ray source in configuration θ - 2θ. Finally, the film surface roughness has been determined on the basis of topography images recorded by tapping AFM on a scanned area of 1 μm × 1 μm.

Friction force measurements were performed by lateral force microscopy using DLC covered AFM tips and DLC covered silicon wafers. The friction curves, *i.e.* variation of lateral force during forward and backward movements of the AFM tip on the probe surface, were recorded for various loading force values at constant movement speed of 1 μm/s. The measurements were carried out in humid air (the relative humidity has been measured by a precision hygrometer HM 34 from Vaisala, Finland) and in argon flow (null relative humidity). The lateral force signal has been calibrated by analyzing the curves of the lateral force versus on the normal loading force acquired on the tilted surfaces of a standard silicon grating sample (TGG 1 from NT-MDT) [13]. The average friction force has been computed as the ratio between the area of the friction loop curve and the total forward and backward moving distance [14]. The standard deviation value of the friction force has been computed based on lateral force variations during the forward and backward movements of the AFM tip. An example of the friction loop is provided in supporting material available. The measurements were made by steadily decreasing the normal loading force towards negative values until the AFM tip detached from the sample surface. The AFM tip-sample adhesive force in humid air and argon has been measured by acquisition of force curves (variation of tip-sample interaction force during vertical advance and retract movements of the AFM tip) taken on a matrix of 10 × 10 points on a square of 1 μm × 1 μm on the flat DLC surface.

3. Results and discussion

Fig. 1a) shows the profiles of an AFM tip before and after DLC thin film deposition, as they resulted by deconvolution of sharp edge images of the standard grating sample [11]. This result is confirmed by the scanning electron microscopy images of the AFM tip before and after DLC deposition, which are shown in Fig. 1b). As expected, the tip curvature increased with about 20 nm, a thickness roughly equal to the thickness of the DLC film deposited on flat surface of silicon wafers. This proved that the deposition was isotropic and conformal, fact that is explained by the frequent collisions between sputtered atoms and argon atoms in the deposition chamber (the mean free path of carbon atoms was estimated to 1.5 cm, which is smaller than the target-substrate distance of 10 cm). A topography image of 1 μm × 1 μm area of the DLC thin film deposited on silicon wafer is shown in Fig. 2. The image shows a smooth DLC surface with the root mean square roughness of 0.27 nm. The X-ray diffraction pattern of the deposited DLC thin films indicated a completely amorphous structure. The chemical structure of the film surface has been characterized by XPS. Fig. 3 shows the core level C 1 s XPS signal and its deconvolution into C − C sp^2, C − C sp^3 and C = O Gaussian–Lorentian peaks. The sp^2 (at 284.4 eV) and sp^3 (at 285,3 eV) peaks were fitted considering their energy separation gap to be 0.9 eV [15, 16]. Deconvolution of the core level C 1 s XPS pick determines densities of 29.2% for sp^3 bonds, 61.3% for sp^2 bonds, and 9.45% for C = O bonds [17]. Incorporation of oxygen into the film surface is due to oxidation of surface carbon atoms after the film was taken out from the discharge chamber and entered in contact with atmospheric air. This surface oxidation effect is favored by the fact that our DLC thin films were hydrogen-free and, thus, likely with a large number of surface dangling bonds. Presence of polar C = O bonds on the DLC thin film surface is in agreement [18] with the results of water contact angle measurements, which revealed values around 65°. The hydrophilicity of these hydrogen-free DLC thin films has a strong effect on adhesion and friction forces. Indeed, the AFM measurements of friction and adhesion forces between DLC covered AFM tip and DLC covered silicon sample showed a strong dependence of these forces on humidity. Fig. 4 shows the plots of friction force dependence on the normal loading force in humid ambient air (relative humidity, RH, of 48%) and in argon (RH = 0%). The plots show that, at large values of the normal loading force, there is no dependence of friction force on the measurement medium. However, at small values of the normal loading force, the friction force in humid air was much smaller than the friction force in argon atmosphere. Moreover, in this region the friction force cannot be fitted by any theoretical model of single-asperity contact friction. Single-asperity contact friction models are based on the assumption that in absence of ploughing the friction force is proportional to the contact area [19], $F_f = \tau \cdot A$, where τ is the contact share stress and it is regarded as a constant that depends on surface properties and medium. Then, the friction force dependence on the normal loading force is related on the dependence of A on normal loading force. This dependence is described by theoretical models of adhesive contacts between elastic bodies as the Johnson–Kendall–Roberts (JKR) [20], Derjaguin–Muller–Toporov (DMT) [21], or Maugis–Dungale (MD) [22] models. The Fig. 4 shows also a fit of the experimental friction force data measured in humid air to the DMT model. The fit has been performed only for large values of the normal loading force (values larger than the absolute value of the pull-off force), where the experimental data fit well the theoretical model. For low values of the loading force, the experiment