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Femtosecond laser microstructuring of diamond-like nanocomposite films

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ABSTRACT

We report on femtosecond laser surface modification and microstructuring of diamond-like nanocomposite (DLN) films (a-C:H,Si:O), and investigation of the frictional properties of laser-micropatterned DLN films on the nano, micro and macroscale. DLN films of 2–3 μm thickness were irradiated using a femtosecond laser (wavelength 1030 nm, pulse duration 320 fs, pulse repetition rate 101 kHz) to produce periodic linear micropatterns over the areas of 40 mm^2. Laser irradiation was performed at low fluences (below the single-pulse ablation threshold) corresponding to the conditions of surface graphitization and incipient ablation developing during the multipulse irradiation. Frictional properties of laser-micropatterned DLN films were studied using (i) lateral force microscopy (LFM) and (ii) ball-on-flat tribometer under linear reciprocating sliding against 100Cr6 steel and Si_3N_4 balls. The LFM measurements revealed significant changes in the friction behavior of the laser-patterned films during transition from nano to microscale, demonstrating much lower friction forces within laser-graphitized strips than on the original film. Such microfriction behavior was attributed to (i) higher hydrophobicity of laser-graphitized nanostructured surface and (ii) strong influence of capillary forces of adsorbed water layers on friction under the 'nano' loads. Macroscopic friction properties of the fs-laser-patterned DLN films were shown to depend on the friction pair (DLN vs steel ball, DLN vs Si_3N_4 ball), both at the initial stage of sliding and during prolonged sliding tests.

1. Introduction

Laser ablation processing with ultrashort (femtosecond, picosecond) pulses is advantageous for surface microstructuring of thin diamond-like carbon (DLC) films due to decreased thermal effects, leading to lower thickness of graphitized surface layers [1] and laser-spalled layers [2] as compared to irradiation with longer nanosecond pulses. Also, an important feature of the DLC surface modification is the formation of periodic surface nanostructures (ripples) occurring on the graphitized DLC surface during fs-laser ablation [3,4]. All the surface modifications (micropatterning, graphitization, nanostructuring) aimed at optimizing the frictional properties of DLC coatings have demonstrated promising results to be very dependent on various experimental parameters including DLC film properties, laser irradiation parameters, friction couple under study, and tribotesting conditions [5–7]. Firstly, the thickness of DLC films is to be of several microns (the thicker the better) to allow the surface micro-dimples with a satisfactory aspect ratio to be produced by laser ablation. Such 'thickness requirement' has proved to be really a big problem for laser surface micropatterning of hydrogenated DLC (a-C:H) films of 1-μm thickness [5]. The solution of the above problem and rapid progress in laser interference patterning of tetrahedral amorphous carbon (ta-C) films (of thickness larger 2.5 μm) for tribological applications have recently been demonstrated [8–10] using UV nanosecond-pulsed lasers. The effect of ns-laser surface graphitization on reducing the friction coefficient of a-C [11], a-C:H [12] and ta-C [12, 13] films is strongly pronounced on the micro and nanoscale. Using friction force microscopy testing in ambient air, it is found that the laser-produced graphitic layer acts as a solid lubricant during sliding of Si and diamond-coated tips on the DLC film surfaces [12,13]. However, the positive effect of the surface graphitization on friction can be reversed by nanoscale topography changes and enhanced surface roughness occurred as a result of laser-induced microspallations in DLC films [14]. In case of fs-laser processing of DLC films, the relative role of the surface graphitization and nanostructuring in the friction reduction is not completely clear because the improved friction behavior was observed only for certain friction pairs under high load sliding conditions [6,7]. The second specific factor of fs-laser processing of DLC films is concerned with relatively low light absorption in the coatings. Advanced fs-laser systems operate usually at the fundamental wavelength of about 1 μm at which the absorption coefficient of the laser radiation for various DLC films is below 10^4 cm^{-1} [15] (~3×10^3 cm^{-1} for

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the films studied in this paper). This makes a multipulse regime of fs-laser irradiation at low fluences very suitable to induce gradual structural modification (graphitization) followed by developing ablation and nanostructuring of the DLC surface [16]. Importantly, the laser microprocessing with a Gaussian beam at low fluences 'automatically' reduces the size of produced micropatterns (relatively to the laser spot size at the level $1/e^2$ of the maximum intensity) which is defined by the graphitization temperature profile across the laser spot.

In this paper we focus on femtosecond-laser surface modification and microstructuring of diamond-like nanocomposite (DLN) films (a-C:H,Si:O), and investigation of the frictional properties of laser-micropatterned DLN films on the nano, micro and macroscale. At first we present data of the elastic properties (hardness, Young's modulus, internal stresses) of DLN films in dependence of growth conditions and film thickness to show that laser micropatterning of relatively thick DLN coatings is feasible. Then, we study the characteristics of fs-laser interaction with DLN films and laser patterning under the conditions of surface graphitization and incipient ablation developing during the multipulse irradiation. Frictional properties of periodic linear micropatterns (laser-graphitized strips with nanostructured surface) are studied using (i) lateral force microscopy (LFM) and (ii) ball-on-flat tribometer under linear reciprocating sliding against 100Cr6 steel and Si_3N_4 balls. The LFM examinations with nano- and micro-sized Si tips (tip radius of 10 nm and 1.5 μm) have revealed considerable differences in the friction behavior in the laser-patterned films under very low loads (tens of nN). The transition from nano to microscale is characterized by much lower friction forces within laser-graphitized strips than on the original film surface, attributed to enlarged hydrophobicity of laser-graphitized nanostructured surface and strong influence of capillary forces on the effective load and friction forces outside the laser strips. Experimental data of the effect of friction pair (DLN vs steel ball, DLN vs Si_3N_4 ball) on macroscopic friction behavior over the fs-laser-patterned surface are also presented and its correlation with the LFM findings is discussed.

2. Experimental details

DLN films were grown on Si substrates using a plasma-assisted chemical vapor deposition from a polyphenylmethyl siloxane vapor [17,18], the pressure was about 10^{-2} Pa. The high-frequency (1.76 MHz) potential applied to the substrate holder provided the appearance of a negative constant bias voltage (U) on the substrate. The bias voltage was in the range from −100 to −700 V. The film growth rate was 1–2 μm/h, and the film thickness ranged from 1 to 10 μm. The film composition determined by electron probe micro-analysis was [C] = 74–80%, [O] = 9–12%, [Si] = 11–14% at., correlating with the ranges of DLN compositions reported elsewhere [17]. The content of hydrogen was in the range of 0.1–0.4 of the atomic concentration of carbon, with the typical composition of DLN coatings being around $(CH_{0.15})_{0.7}(SiO_{0.4})_{0.3}$ [17,19].

Laser surface micropatterning of 2–3 μm-thick DLN films on Si substrates was carried out using a 5 W SATSUMA femtosecond laser (from Amplitude – Systèmes) generating pulses of $\tau = 320$ fs duration at the wavelength $\lambda = 1030$ nm. The average power was varied from 30 to 1000 mW at the pulse repetition rate $f = 101$ kHz, corresponding to the range of the laser pulse energy (ε) from 0.3 to 10 μJ. The laser spot radius was $w_o = 21.4$ μm, and the beam quality $M^2 < 1.44$. A high precision scanner was used to control the scanning beam velocities (V_s) from 10 m/s down to 0.05 m/s. The high scanning velocity (10 m/s) was applied for the single-pulse irradiation with the spacing between spots equal to $V_s/f = 99$ μm, while the low scanning velocities from 0.8 down to 0.05 m/s were used in the multipulse irradiation regime to vary the effective number of pulses from N ~ 5 to 80. In the multipulse regime, periodic linear micropatterns were produced over the surface areas of 2 mm × 20 mm for subsequent tribological testing. The laser-patterned samples were examined using optical microscopy (OM), scanning electron microscopy (SEM), and atomic force microscopy (AFM). The structure modifications of the DLN films were studied using Raman spectroscopy (Ar-ion laser, excitation wavelength 514.5 nm).

The surface relief and friction properties of laser-patterned DLN films on the nano and microscale were studied with an atomic force microscope of the NTEGRA Spectra system (NT-MDT) using a lateral force mode. AFM Si probes with the spring constant of 2 N/m and the tip radius of $R_{tip} = 10$ nm and $R_{tip} = 1.5$ μm were used. The tip scanning speed was 80 μm/s in LFM measurements. The LFM measurements were carried out in ambient air at relative humidity RH = 45–50% and room temperature $T = 25$ °C.

The hardness (H_{IT}) and Young's modulus (E_{IT}) of DNL films were measured by nanoindentation using a nanoindenter NHT2-TTX (CSM Instruments SA). Tribological tests of the as-grown and laser-micropatterned DLN films were performed using a ball-on-flat tribometer TRB-S-CE-0000 (CSM Instruments SA) under linear reciprocating sliding against 100Cr6 steel and Si_3N_4 balls of 6-mm diameter. The test conditions were as follows: (i) the stroke length 4 mm, (ii) the normal load 0.5 N, (iii) the sliding speed from 0.01 to 5 cm/s, (iv) the number of cycles from 10 to 4×10^4. The friction measurements were carried out in air at RH = 50% and room temperature $T = 25$ °C.

3. Results and discussion

3.1. Nanohardness and elastic modulus of DLN films

In early paper [17] it has been proposed to consider the DLN film structure consisting of two atomic-scale networks – a diamond-like carbon a-C:H network and a glass-like a-Si:O network. Such specific film structure of interpenetrating amorphous networks was supposed to be responsible for lower internal stresses, higher temperature stability, improved adhesion of the DLN coatings as compared with hydrogenated a-C:H films [17,19,20]. For our DLN samples the internal stresses, increasing with the bias voltage, do not exceed the value of 250 MPa for the films of the highest Young's modulus obtained at $U = -(400–500)$ V.

In nanoindentation tests, the hardness H_{IT} and reduced elastic modulus (E^*) of the DLN films of different thickness (from 1 to 9 μm) were determined from the load/displacement curves at the maximum load of 1 mN using a Berkovich diamond indenter. The Young's modulus was derived from $E_{IT} = E^*(1\text{-}\nu^2)$, taking the Poisson coefficient of $\nu = 0.2$ for the DLN films. Fig. 1a shows the dependence of the DLN hardness and Young's modulus on the bias voltage (from −150 to −700 V) during deposition. The maximum values $H_{IT} = 28$ GPa and $E_{IT} = 190$ GPa were achieved at $U = -400$ V.

As the internal stresses increase with the bias voltage, there is a compromise choice between increasing the hardness and reducing the stresses to grow hard DLN coatings as thick as possible. The bias voltage of $U = -200$ V satisfied the above requirement, and it was applied to deposit DLN films with low internal stresses (of about 100 MPa) and thickness of up to ~10 μm. The data of the DLN film hardness versus thickness are plotted in Fig. 1b. It is found that the DLN films deposited at $U = -200$ V show identical elastic properties with thickness (from 2 to 9 μm): the nanohardness is in the range of $H_{IT} = 22–25$ GPa and the Young's modulus is $E_{IT} = 135–140$ GPa, that makes the DLN coatings very promising for laser patterning applications in tribological systems. In this work, a sample of 2.4-μm-thick DLN film, deposited at $U = -400$ V on Si substrate and characterized by $H_{IT} = 28$ GPa and $E_{IT} = 190$ GPa, was used in fs-laser micropatterning experiments.

3.2. Femtosecond laser micropatterning of DLN films

For single pulses, laser surface interaction with hydrogenated DLC films is characterized by three main processes – graphitization, spallation and evaporation (ablation) – clearly observable in progressive