MODIFICATION OF SURFACE AND TRIBOLOGICAL PROPERTIES OF DLC FILMS
BY ADDING SILVER CONTENT

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ABSTRACT
The incorporation of silver into the diamond-like carbon (DLC) coatings has shown excellent potential in various applications; therefore the surface and tribological properties of silver-containing DLC thin films deserve to be investigated. In this study we have deposited silver-containing hydrogenated and hydrogen-free DLC coatings by plasma immersion ion implantation and deposition (PIII-D) methods. Atomic force microscopy (AFM) and nano-scratch tests were used to study the surface and tribological properties. The silver incorporation had only slight effects on hydrogenated DLC coatings. However, the incorporation of silver has significant effect on hydrogen-free DLC of smoothing the surface and increasing the surface energy. Those effects have been illustrated and explained in the context of experimental results.

INTRODUCTION
While the effect of adding silver to DLC coatings has been tested to be beneficial in a variety of applications [1-8], the tribological properties of these films are not yet completely understood. In order to justify the application of silver-containing DLC coatings in various applications, surface analysis and tribological property characterization were carried out for silver-containing DLC coatings deposited by PIII-D methods. In the previous work the composition, microstructure, mechanical and biological properties of DLC-Ag samples have been characterized in details [1]; this manuscript focuses on the surface characteristics of DLC-Ag coatings. The notation of a-C:H and a-C are referred to hydrogenated and hydrogen-free DLC; the corresponding silver-containing samples are referred to a-C:H/Ag and a-C/Ag. AFM was used to image the coatings' surface topography. Mechanical tests of nano-scratch were carried out to characterize the coatings’ tribological properties.

EXPERIMENTAL PROCEDURES
The DLC-Ag composite coatings were grown by PIII-D methods. The hydrogenated films were grown by methane reactive precursor together with pulsed cathodic arc discharging from a silver target; the hydrogen-free films were grown by alternating arc pulses from two separate cathodic arc discharging sources of carbon and silver [1]. A thick layer of chromium was deposited firstly onto the silicon substrate as a buffer layer. The coatings surface topography was measured by AFM with a Veeco Digital Instruments Dimension 3100 operated at tapping mode with a drive frequency of 259.332 kHz and scan rate of 2 Hz. The tribological properties of the deposited coatings were studied by nano-scratch tests with a surface force microprobe apparatus (Hysitron) operated in a controlled environment of temperature ~25 ºC and relatively humidity ~45 percent [9]. The tests were performed with a diamond tip of ~ 20 µm nominal radius and 400 nm/s scratching speed. The coefficient of friction (COF) was measured as the ratio of the measured friction force to the applied normal force.

RESULTS AND DISCUSSION
The surface topography measured by AFM is shown in Fig. 1. On the top surface of a-C:H, the grain-like morphology was probably because the deposited DLC followed the pre-existing surface structure, reflecting the crystalline chromium feature underneath [10]. A-C:H/Ag had finer grain-like surface structure than a-C:H possibly due to the silver nano-crystalline particles that affected the on-growth of the following DLC. For a-C, the energetic carbon ions from cathodic arc discharging smoothed the surface by re-sputtering and diffusion effects. The 3D-growth of silver content also has the smoothing effect [11]; therefore a-C/Ag had the lowest roughness because of the combined smoothing mechanisms. The RMS roughness values of all samples are summarized in Fig. 2.
Fig. 1 The AFM image of (a) a-C:H, (b) a-C:H/Ag, (c) a-C and (d) a-C/Ag with the scan size of 1 × 1 µm².

Fig. 2 The root-mean-square (RMS) roughness of the four samples with the scan size of 1 × 1 µm².

Fig. 3 The average COF of the four samples with different normal loads.

The COF measured by nano-scratch tests have been plotted in Fig. 3. The COF was observed to have less average value and less fluctuation under higher applied loads. The average COF decreased with applied load because they were calculated only with measured normal and lateral forces; the adhesion force between the tip and sample surface was not counted. When the normal applied load was small, the adhesion force was comparable to the load and raised the apparent COF value [12]. A study involving contact geometry and adhesion force predicts that the COF is inversely proportional to the cubic root of the normal applied load, i.e., COF \( \propto P^{-1/3} \), where \( P \) is the applied load [13]. The frictional force may come from two different mechanisms: adhesion that is by the elastic deformation of the surfaces, and abrasion (plowing) which involves plastic deformation. The surface imaging by AFM after the nano-scratch tests did not yield any discernible evidence of permanent deformation, suggesting that the scratching was predominantly elastic. The COF under high loads were below 0.2, which is in agreement with the prediction of the classical adhesion theory of friction [14]. Generally the adhesion force is proportional to the surface energy of the two contacting surfaces, which depends on the number of dangling bonds on the surface and the degree of surface reconstruction [15]. Hydrogen decreases the DLC surface energy [15]; while the exposing silver on top surface increases the surface energy [2,5,16]. Therefore the chemical composition partially explains the results that hydrogenated films had lower COF than hydrogen-free films, and that silver-containing films had higher COF than pure DLC. The mechanical properties could also contribute to the COF trend. When the external load increases, the plastic shearing (plowing) effect increases and the COF becomes more dependent on the materials properties instead of the external load; under this mechanism COF decreases with the applied load [17]. The surface roughness is inversely proportional to COF under light contact region because low roughness induces more adhesion force by non-contacting (proximity) surface asperities [18,19]. The surface roughness effect is best illustrated by a-C/Ag that had the lowest roughness and highest COF. Further studies are expected to explain the tribological properties under a wide range of loads and possible wear particle formation of DLC-Ag films.

CONCLUSIONS

Both a-C:H/Ag and a-C/Ag coatings have been tested by AFM and nano-scratch in relation to the a-C:H and a-C coatings. By comparison, silver had more pronounced effect on hydrogen-free DLC than hydrogenated DLC in terms of surface roughness and surface energy. The silver and hydrogen content in the sample have opposite effect in the tribological properties because of their different contribution to the surface energy. The COF difference between samples has been analyzed by friction mechanisms.
REFERENCES


