

# Microstructure of amorphous diamond-like carbon thin films and changes during wear

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Received 10 May 2004; accepted in revised form 10 April 2005

Available online 13 June 2005

## Abstract

Using scanning and transmission electron microscopy, we investigate the microstructure of diamond-like carbon (DLC) thin films deposited in an electron-cyclotron resonance plasma. During *pin-on-flat* wear experiments, the amorphous DLC films are found to be a source for formation of transfer film and wear track debris with composite microstructure. The transfer film is observed to consist of an amorphous matrix with dispersed microcrystalline and tubular particles. The debris from the wear track represents separated bundles of aligned tubular particles and clusters of microcrystalline particles. The lowering of the coefficient of friction measured during the wear experiments is related to the formation of the composite transfer film and its stable low value—to the possibility that the randomly oriented tubular particles from the transfer film engage in rolling friction in the process of their organization into aligned bundles.

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**Keywords:** Diamond-like carbon; Wear mechanism; Ultra thin film; Amorphous; Friction

## 1. Introduction

Solid lubricants, such as graphite and DLC films, are of great technological and industrial significance because of their tribological properties that combine excellent wear resistance with very low coefficient of friction [1–4]. The use of DLCs as coatings on high-precision components with close mechanical tolerances, e.g., in magnetic storage applications [5], and on novel micro- and nanoscale mechanical devices [6] has become particularly important recently. This use stimulated an intensive investigation to understand the macroscopic and microscopic mechanisms of wear in these materials [1]. Macroscopic wear of graphite, diamond, and thin films of these materials is relatively well understood [1,4]. Graphite has good lubricating performance in air due to its layered structure that allows wear via sliding and shearing of individual layers. There is some

evidence to show that rolling friction might also play a role in graphite lubrication, since, along with graphitic flakes, carbon-based rollers were observed in the wear track [7]. Water vapor effectively enhances lubrication in graphite and carbon-based materials, and thus it appears that improved molecular mobility and oxidation processes play a role in the lubricity of these materials [8]. Diamond wear has been found to proceed via formation of waxy hydrocarbon debris that acted as lubricating material [9,10]. The debris produced in vacuum is found to contain mainly amorphous carbon and small diamond particles. Good overview of DLC wear mechanism and diamond films is discussed by Grill [1,2] and studied by other authors [11–15]. The most common theory of the wear mechanism for amorphous hydrogenated DLC (*a*-C:H) films includes contribution from two components: (i) hydrogen on the film surface may act as a gas-phase lubricant that passivate dangling bonds on the film surface that permit only weak interactions at the sliding interface and (ii) friction-induced shear forces that help the breaking C–H and C–C bonds and the

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transformation to graphitic structure. This carbon rich material participates in the formation of a transfer film on the counter wear surface that is instrumental to the lubrication process [16]. The mechanical performance of *a*-C:H films is dependent upon the environment because water/oxidation might prevent the formation of the transfer film. One way of achieving this is by understanding the microstructure of the films and the changes that occur in it, the transfer film and the debris that form in the wear process. In this paper we use transmission electron microscopy (TEM) to study the microstructure of *a*-C:H films and its changes during wear process. We investigate the debris and transfer film formation and their microstructure.

## 2. Experimental procedure

The *a*-C:H films were prepared by electron-cyclotron resonance plasma-enhanced chemical vapor deposition (ECR-CVD) using methane and hydrogen precursor gases, as described in [17]. ECR-CVD processes have distinct advantages for ultra-thin films preparation because of their low deposition rates and their low operating pressure ranges of  $10^{-4}$ – $10^{-2}$  Torr. However the process is very efficient in the 2.45 GHz operating range and generates a high-density plasma which favors diamond growth. One important aspect of this process is that it is possible to grow diamond at temperatures below 500 °C, even as low as 300 °C. The films used in the wear mechanism studies here were 50 nm thick and were deposited on Si(100) substrates [17]. The X-ray photoemission spectroscopy (XPS) was performed using a 1485 eV Al K $\alpha$  X-ray source. The X-ray spot size is approximately  $0.5 \times 0.7$  mm<sup>2</sup>. A Survey scan was performed for all the samples to identify the small amount of dopants or contamination in the films, followed by a high-resolution scan of each of the species. An analysis of the chemical composition of the virgin surface and after sputter cleaning was performed. A nanoindenter, a widely accepted tool for measuring the mechanical properties of thin films and small volume material, in dynamic contact mode was used at an average maximum depth of 10–12 nm and maximum load of 0.06 mN [18,19]. The coefficient of friction was determined during wear measurements of the films. The wear measurements were performed using a *Pin-on-Flat* reciprocating test with a 1.5875 mm diameter sapphire ball (Young's modulus of 345 GPa) ultrasonically cleaned in acetone, followed by isopropanol, and nitrogen dried. A normal load of 1 N (Hertzian stress of 1.74 GPa [20]) was applied and linear sliding speed of 1 mm/s with 2 mm track length (frequency of 0.5 cycle/s) for 5.5 h (5000 cycles) at constant ambient conditions of 23 °C and 20% RH was used, this was monitored throughout the entire test duration. In a separate experiment using the same conditions, film failure occurred after 9.5 h. The surface roughness and wear track profile is measured using a white light optical interferometer technique with a height reso-

lution of 3 nm and lateral resolution of approximately 100 nm [20]. The surface roughness was measured from a  $1 \times 1$  mm<sup>2</sup> area, and the entire wear track area was stitched from smaller  $0.5 \times 0.5$  mm<sup>2</sup> area scans using an auto-stage with calibrated lengths. The mechanical profiler was used to confirm the optical profile measurements.

The wear tracks were studied using an environmental scanning electron microscope (SEM) at 30 kV with a working distance of 9 mm for imaging and to identify all impurities. The electron energy was then lowered to 3 kV to resolve the lighter elements with less penetration depth. The detailed microstructure of the DLC films prior to wear testing was investigated using cross-sectional TEM (XTEM). The XTEM specimens were prepared by tripod polishing, a method particularly suitable for obtaining large, homogeneously thin electron transparent regions. Polishing was followed by brief ion-milling in a BalTec Res 100 ion mill at a sputtering angle of 4° to minimize any structural modifications due to specimen preparation. The samples were examined in a Philips CM200 TEM operating at 200 kV. The microstructure of the debris and the transfer film formed during wear was also examined using TEM. Material from the wear track as well as from the sapphire ball was picked up and transferred to the lacy carbon TEM sample grid by simply contacting the two surfaces.

## 3. Results

Before the wear experiments were carried out, the DLC films were imaged using XTEM to observe the microstructure and verify the film thickness. The results of the XTEM investigation of a 50 nm thick DLC film on Si(100) substrate is shown in Fig. 1. In order to distinguish the surface of the film from the carbon-based glue used to prepare the XTEM sample, gold was deposited using radio frequency (RF) sputtering at room temperature as a marker. The gold does not form a continuous layer but clusters on

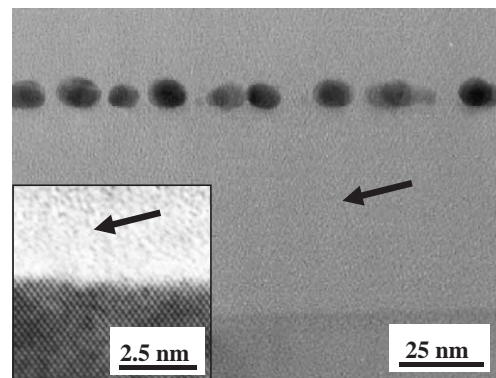


Fig. 1. Cross-sectional transmission electron microscopy (XTEM) image of 50-nm-thick *a*-C:H film (as indicated by arrows) on Si (100) substrate. The dark contrast stems from gold clusters marking the surface of the film. The insert shows a high-resolution XTEM image from the region near the amorphous film/crystalline substrate interface.

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