



Adsorption of polar molecules on diamond-like carbon films with different trapped charge densities



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ARTICLE INFO

Article history:

Received 30 November 2015

Received in revised form 15 February 2016

Accepted 1 March 2016

Available online 3 March 2016

Keywords:

Diamond-like carbon

Trapped charge

Adsorption

Polar molecules

ABSTRACT

This work investigates the effect of trapped charge densities present in diamond-like carbon films (DLC) on adsorption of polar molecules on the film surface. Hydrogen-free and hydrogenated DLC films with different hydrogen/carbon contents were produced using filtered-cathodic arc sputtering (FCA-sputtering) and radio-frequency plasma enhanced chemical vapor deposition (RF-PECVD) techniques, respectively. After treating the as-prepared films in a dilute solution of dipropylene glycol monomethyl ether, adsorption of such molecules was found throughout the film surface. Capacitance–voltage (C–V) measurements have shown that the DLC films with lower hydrogen/carbon content inherently have larger trapped charge accumulations within their structures. A charge density of 1600 nC/cm² was measured in a DLC film with a lower hydrogen/carbon content (produced from C₂H₄ and Ar precursors), while a much smaller charge density of 64 nC/cm² was measured in a DLC film with a higher hydrogen/carbon content (produced from 10% CH₄ and 90% H₂ precursors). A correlation between charge densities and the degree of polar molecule adsorption was observed. Films with higher charge densities appeared to be more prone to polar molecule adsorption.

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1. Introduction

Diamond-like carbon (DLC) is a class of solid lubricants used in various industrial applications for their excellent mechanical and tribological properties, including high hardness and their ultra-low friction coefficient [1–4]. DLC has been used as hard coating material on carbides [5], steel tools [6] and in hard disk drives to minimize wear between read/write heads and magnetic media [7–8]. DLC coated parts are usually lubricated or treated with some chemicals in certain manufacturing processes. An understanding of the factors that affect adsorption of molecules on surfaces of DLC films is crucial for development of devices with functionalities and performance that rely on the interfacial interaction between DLC-coated parts. Adsorption of various oils, alcohols, and other additives on DLC surfaces has been reported [9–18]. Under ambient conditions, dangling bonds on DLC surfaces are believed to be passivated by hydrogen, oxides and hydroxides [19–20]. Additive molecules near its surfaces are then physically adsorbed by hydrogen bonding with the surface oxides and hydroxides. To some extent, these molecules can also be chemisorbed onto DLC surfaces [9–11,20–21]. Tribochemical reactions can further induce adsorption of additive molecules on DLC surfaces. Multiple studies [9–11] reported chemisorption of hexadecanoic acid and hexadecanol molecules on DLC films induced by tribological contact between their

surfaces. The passivating surface layers can be removed as a result of wear, which allows creation of new dangling bonds. These bonds tend to react with unbound hydrogen and other molecules. Similarly, hydroxylation of the friction surfaces due to a tribochemical reaction with alcohol hydroxyl groups was also suggested in studies where glycerol mono-oleate [12] and polyhydric alcohols [13] were used as additives.

Recent work addressing the lubrication mechanisms of oils, alcohols and other additives on DLC allows us to gain more understanding of the adsorption mechanisms on DLC surfaces. The influences of these additives on the tribological performance of DLC films have been extensively investigated [9–18,20–25]. The characteristics of both the DLC films and the additives were found to have an effect on the tribological performance of coatings. For example, a DLC film with different dopants or hydrogen contents can result in different tribochemical reactions at the lubrication boundary between DLC materials and particular additives [14,20]. For boundary-lubricated additives, the performance of the DLC coatings may also depend on their viscosities, degrees of unsaturation, and polarity [18,23–25].

Although understanding the lubrication effects of DLC coatings has improved drastically in the past decade, a systematic investigation of the nature of DLC's surface state and its influence on adsorption of molecules is still necessary. In general, the properties of DLC films produced from different fabrication processes are dissimilar and dependent on their microstructure and chemical composition [26–27]. Several research studies have shown that factors such as the ratio between sp³

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and sp^2 hybridized bonds or hydrogen content in the films can significantly affect their tribological properties [28–30]. In this regard, surface properties of DLC films may also be altered by varying deposition conditions. Specifically, DLC surface energies are known to depend on several different parameters, e.g., dispersion, polar nature, electron acceptor and electron donor, among others, which are related to the films' physical and chemical structures. While the effects of dispersion and polar components on the adsorption of polar molecules have been extensively studied [31–32], reports of the effects of charge defects, such as trapped charges on the adsorptions of polar molecules on DLC films, are sparse. These trapped charges, commonly found in dielectric materials [33–34], may be related to electron acceptor/donor components of the total surface energies of DLCs.

This work investigates the surface polarity-induced by trapped charges inherent within the structure of DLC films. Capacitance–voltage (C–V) measurements were used to quantify the trapped charge densities in DLC films that were produced from precursor gases containing different hydrogen contents. We introduce the adsorption of polar molecules on DLC films using a wet chemical treatment process involving a dilute solution of dipropylene glycol monomethyl ether (DGME). We discuss the influence of DLC film surface polarity on the likeliness of a polar molecule undergoing surface adsorption.

2. Experimental

The deposition of DLC films was done on p-type Si substrates (dopant concentration of $3 \times 10^{16} \text{ cm}^{-3}$) using filter cathodic arc sputtering (FCA-sputtering) and radio-frequency plasma enhanced chemical vapor deposition (RF-PECVD) techniques. Samples were divided into 3 groups, 1) hydrogen-free DLC prepared by a FCA-sputtering technique using a pure graphite target, 2) hydrogenated DLC prepared by RF-PECVD using low hydrogen content precursors, and 3) hydrogenated DLC prepared by RF-PECVD using high hydrogen content precursors. The key deposition parameters of these samples are summarized in Table 1. The resulting film thicknesses and permittivity were measured using an ellipsometer (Gaertner Scientific Corporation Ltd., Stokes Waferskan™ Ellipsometer L115S300).

The charge density in DLC films was investigated using capacitance–voltage (C–V) analysis. Metal–insulator–semiconductor (MIS) structures were constructed by sputtering Au metal gates on top of the DLC films. In this experiment, the DLC layers were treated as insulator of the MIS structure. The Au/DLC/Si structures were then placed on Ag electrodes. The structures were subjected to a high-frequency (100 kHz) AC signal superimposed on ramped DC potentials (–25 V to +25 V). Fig. 1 shows schematic representation of the MIS structure. C–V curves were obtained using a setup comprised of LabVIEW programmable instruments, i.e., an LCR meter (Agilent 4263B) and a DC power supply (Agilent E3631A). All C–V measurements were performed in a shielded probe station. Contact angle measurements (FTA 1000 Drop Shape Instrument B Frame) were also performed, where wettability was used to compare the surface polarities among the samples.

Contact angle measurements for DI water drops on different DLC surfaces were performed at room temperature. The samples were exposed to laboratory air for a short period of time and were kept in vacuum-sealed containers. Prior to testing, the samples were

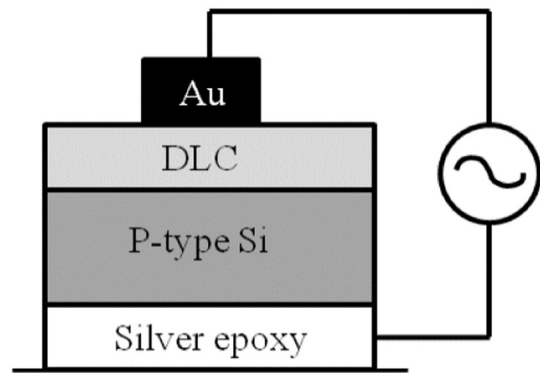


Fig. 1. Schematic representation of the MIS structure used for C–V analysis.

unavoidably exposed to air under ambient conditions and were tested without further cleaning. The contact angles were calculated by aligning a tangent with the drop profile at the point of contact with the DLC surface using drop photographs obtained using a digital camera.

For the chemical treatment process, as-fabricated films were subjected to a dilute solution of dipropylene glycol monomethyl ether (DGME) in de-ionized (DI) water. This polar molecule was selected because it is commonly incorporated as an ingredient in dust removal compounds used for DLC coated parts. The processing steps were carried out as follows: the samples were 1) fully submerged in a 2% DGME solution for 180 s, 2) submerged in a 1% DGME solution for another 180 s, 3) washed in an ultrasonic bath containing DI water for 180 s, 4) rinsed with abundant DI water for 300 s and 5) dried in hot air at 80 °C for 500 s.

Surface topography characterizations of DLC films before and after the chemical treatment process were carried out using field-emission scanning electron microscopy (FE-SEM) (Zeiss Ultra 55) with an accelerating voltage of 0.5 keV. This low accelerating voltage was used in order to minimize the electron interaction volume. Images were recorded using an InLens detector. The samples were characterized with no conductive coating.

3. Results and discussion

3.1. Capacitance–voltage analysis

Fig. 2 shows the equivalent circuit of the MIS structure indicating capacitances in insulator and semiconductor layers.

The total capacitance per unit area can be derived as:

$$C = \frac{\epsilon_{DLC} \epsilon_0}{t + \left(\frac{\epsilon_{DLC}}{\epsilon_S} \right) x_S} \quad (1)$$

where ϵ_{DLC} is the relative permittivity of DLC, ϵ_0 is the permittivity of free space, ϵ_S is the relative permittivity of the silicon substrate, t is the thickness of the DLC layer, and x_S is the thickness of the depletion layer in the substrate. The flat-band condition is generally derived as a condition when the surface potential of the semiconductor is zero,

Table 1
Fabrication techniques and deposition parameters of DLC films.

Sample	Technique	Deposition parameters	Thickness (nm)	ϵ_{DLC}
1. Hydrogen-free DLC	FCA-sputtering	Graphite target/Ar	2	–
2. Low H/C DLC	RF-PECVD	C_2H_4 35 sccm/Ar 12 sccm	10	7.40
3. High H/C DLC	RF-PECVD	CH_4 6 sccm/ H_2 54 sccm	29	4.40

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