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Solvent effect on the formation of self-assembled monolayer on DLC surface between *n*-hexane and Vertrel XF

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Self-assembled monolayers of 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichloro-silane (FDTS) have been deposited on the diamond-like carbon (DLC) film-coated magnetic heads with two different solvents, *n*-hexane and Vertrel XF. In order to investigate the solvent effect on the monolayer formation, a series of FDTS monolayers were prepared by varying the solution concentrations which were respectively characterized by time-of-flight mass spectroscopy, contact angle measurements and atomic force microscopy. Results showed that high density of aggregations were present for the FDTS monolayers using the *n*-hexane solvent, while the monolayer formed on the DLC surface using the Vertrel XF solvent exhibited excellent quality and reproducibility and no aggregations were observed.

1. Introduction

Diamond-like carbon (DLC) films have been widely used as anti-wear and anti-corrosion coatings in hard disk drive systems due to their superior wear-resistance properties even with a film thickness less than 5 nm [1,2]. However, the excellent mechanical properties of DLC can be much seriously impaired due to the presence of "pin holes" on the film surface [3]. For this, self-assembled monolayers (SAMs) are often used as nanolubricant thin films to enhance the performances of carbon overcoats due to their high density, low surface energy and good frictional properties [4]. Therefore, the proper application of a thin lubricant layer on a DLC-coated magnetic head has become one of the most important issues in the fabrication of magnetic media [5,6]. In this regard, dip-coating technique has been widely used for lubricant deposition. However, in the practical applications, a monolayer often forms with a great lot of aggregations [7]. If such aggregations were adhered on the DLC surface, the SAM's anti-friction or anti-stiction performances can be seriously degraded, which will dramatically affect the read–write ratio and even cause the device failure in the hard disk drive (HDD) system. In order to avoid this deficiency, a high-quality monolayer is often required to be prepared by varying the deposition conditions such as solvent, water content, temperature, molecular concentration and so on [8–10]. Solvent has been shown to be one of the critical factors in the formation of self-assembled monolayers [11]. It is well known that the lubricant monolayer thickness is mainly controlled by the pulling-up speed as well as the lubricant concentration in the solvent [12,13]. For such an ultra-thin liquid lubricant dipping, the absorption mechanism will play an important role in the growing process of the monolayers [12]. Thus, the microstructure and surface morphology of the lubricant layer would be expected to depend on the solvents due to their different interactions with the lubricant [14]. However, less work has been performed to determine the role of solvent and its possible impact on lubricant deposition.

In the present work, FDTS lubricants were respectively deposited on the DLC surface as a function of solution concentration. For comparison, two different solvents were used in the dip-coating process. One is the hydrocarbon fluid *n*-hexane, the other is the fluorocarbon fluid Vertrel XF. Effects of the solvent on the monolayer formation are then reported in terms of time-of-flight second ion mass spectroscopy (ToF-SIMS), contact angle and atomic force microscopy (AFM) investigations.

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2. Experimental

2.1. Materials

FDTS (96% purity, 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane) was obtained from Alfa Aesar, a Johnson Matthey Company, which was stored in a nitrogen-contained dry box. Vertrel XF (2,3-dihydrodeca-fluoropentane) was received from DuPont Company, which is a clear and colorless liquid. The properties of Vertrel XF and Hexanes are both summarized in Table 1. In this experiment, all the chemical agents were fresh without any further purification. The test samples are DLC-coated magnetic heads (1235 μm × 700 μm × 230 μm size) with film thickness of about 2 nm. The DLC films were prepared on a filtered cathodic vacuum arc system [15].

2.2. Dip-coating process

In this experiment, a series of FDTS/*n*-hexane and FDTS/Vertrel XF solution was prepared with concentrations of 2000 ppm, 1000 ppm, 700 ppm, 500 ppm, and 200 ppm. Before dipping, the DLC-coated magnetic heads were initially treated by a consecutive cleaning process involving vacuum SFC brush cleaning, isopropanol ultrasonic cleaning, de-ionized (DI) water rinsing and nitrogen purging. Then the samples were fixed in a special fixture and were pre-rinsed in the plain solvent for 2 min. After being dipped into the solution for 5 min, the samples were vertically pulled out from the FDTS solution at a constant speed of 0.5 mm/s. The pulled-out samples were then rinsed in the plain solvent for a second time to remove excess coupling agent. Finally, the samples were heat-treated in a low-temperature oven at 130 °C for 30 min. In this work, all above experiments were conducted at room temperature.

2.3. Monolayer characterization

Time-of-flight second ion mass spectrometer (ToF-SIMS) with a lateral resolution of 0.1 μm and a measuring range in depth from a few angstroms to 2 nm has been used in the analysis of the thin film on the magnetic head surface. Here, the ToF-SIMS characterizations were performed with a PHI TRIFT II instrument, using a Ga+ liquid metal ion source (LMIG) with energy of 15 keV. The vacuum in the chamber was 2×10^{-9} Torr. The measured area is 200 μm × 200 μm.

Water contact angle (CA) measurements were carried out on a VCA-2500XE goniometer. Typically, 0.2 μL DI water was dropped on the sample surface using a syringe, and an average value of CA was obtained by measuring the contact angles for three different samples. The experimental error of the CA values is within 0.1°.

AFM imaging was conducted on a XE-HDD AFM (PSIA Instruments). A G-scanner was used with a maximum scan area of 100 μm × 100 μm. In order to avoid the possible scratching damage, all the AFM images shown in this work were obtained using an etched silicon probe in a non-contact mode.

Table 1
Physical properties and specifications for Vertrel XF and hexanes

Property	Vertrel XF	Hexanes (95% *n*-hexane)
Molecular weight	252	86.18
Boiling point	55	69
Liquid density (g/cm^3)	1.58	0.6603
Fluoropentanes/hexanes	99.9 min.	99.6 min.
Moisture (ppm wt)	50 max.	10 max.

3. Results and discussions

3.1. ToF-SIMS characterization

ToF-SIMS is a very versatile analysis technique due to its very high surface specific sensitivity. It was used to characterize the FDTS monolayer on the surface of magnetic heads [16]. Both positive and negative ion mass spectra were measured to obtain the molecular information on the sample surface. Fig. 1a and b shows a typical positive and negative secondary ion spectrum of FDTS monolayer on mass range from 0 amu to 200 amu (atomic mass units). In this spectra, these dominant peaks were located at 12 amu, 19 amu, 31 amu, 50 amu, 69 amu, 100 amu, 119 amu, 131 amu, corresponding to fragments of C^+, F^-, CF^+, $CF_2{}^+$, $CF_3{}^+$, $C_2F_4{}^+$, $C_2F_5{}^+$, $C_3F_5{}^+$, respectively, which confirms the adsorption of FDTS monolayer on the magnetic head surface.

3.2. Contact angle measurements

Fig. 2 shows the measured CA values for the monolayers deposited from FDTS/*n*-hexane and FDTS/Vertrel XF solution, respectively. For the bare DLC surface, the initial water contact angle is 75°. As the FDTS concentration increased, the contact angle rose up and saturated at 110–115°. This excellent hydrophobic nature on the sample surface indicated a complete or uncompleted monolayer was formed. Bunker et al. [17] have reported that the calculated CA value of a complete monolayer was 115° for a fluorocarbon monolayer on silicon substrate. However, Choi et al. [5] found the CA values were saturated at 110° for the DLC-coated samples dipped in the FTE/ethanol solution. Such a difference in

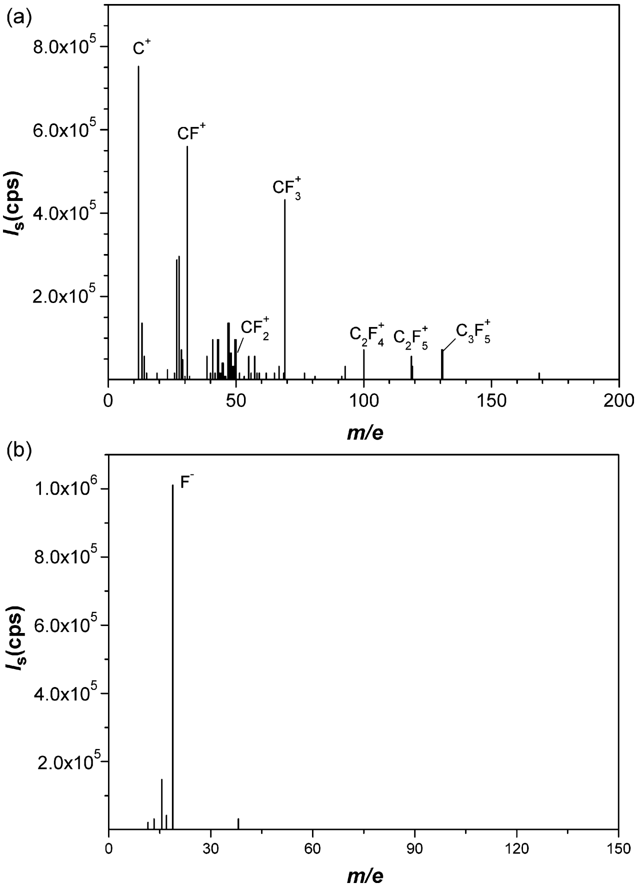

Fig. 1. Typical positive and negative secondary ion spectrum of FDTS monolayer.