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Nano- and microtribological characterization of silanes deposited on cobalt substrate

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ABSTRACT

In this paper, vapor phase deposition was used to grow fluoroalkylsilane films on cobalt surface. The films were characterized by contact angle analyzer for hydrophobicity and X-ray photoelectron spectroscopy (XPS) for identification of fluoroorganic monolayers deposited on the surfaces. Adhesion and friction measurements were performed using atomic force microscope (AFM) and compared with measurements made by microtribometer operated in millinewton (mN) applied load range.

Nano- and microtribological measurements show that cobalt modified by fluoroalkylsilanes has lower adhesion and coefficient of friction. The investigation also indicates a decrease of friction coefficient with increasing fluoric alkyl chain length. Covalently bonded fluoroalkylsilanes with longer alkyl chains are found to be a prime candidate for practical use as a lubricant.

1. Introduction

Cobalt based alloy substrates have been extensively investigated for several years because of their potential application in many technological fields. They are used as new materials in microelectromechanical systems (MEMS), especially in magnetic actuators field. They are also used in biomedical implants because of their excellent mechanical properties, corrosion resistance and biocompatibility [1].

Large adhesion, friction and wear in the case of MEMS can cause some limitations in their production and potential use. For the purpose of better mechanical and chemical properties, their surfaces are modified with lubricants. An ultrathin lubricant film minimizes adhesion, friction and wear between surfaces in contact. One group of the lubricants used in MEMS are silanes. Fluoroalkylsilanes as a self-assembled monolayer (SAM) consist of three building groups: a head group that reacts with a substrate, a backbone molecular chain group, and a terminal group that interacts with the outer surface of the film [2,3]. Fluoroalkylsilanes are formed through hydrolysis reactions, to make bridging siloxane bonds that anchor to the surface and also crosslink to form stable interconnections with adjacent molecules [4–10]. In recent research, the modification of surface properties and functionality through changes in the terminal group has been studied [11–13]. The terminal group determines the surface character. The change of the surface character from hydrophilic to hydrophobic results in decreasing capillary force, better thermal stability, enhanced wear resistance and reduced van der Waals interactions. Such change could be achieved by the coverage of the substrate with monolayer of fluoroalkylsilanes [14–17]. Maboudian et al. [18] reported that perfluorinated silanes show an increase of thermal stability in comparison with nonperfluorinated silanes.

In this paper, we report a comparative study of the nano- and microscale properties of nonperfluorinated and perfluorinated silanes with different carbon chains length. Properties of fluoroalkylsilanes on Co/Si, such as hydrophobicity, surface free energy, adhesion and friction, are evaluated by contact angle measurements, atomic force microscopy (AFM), microtribometry, and X-ray photoelectron spectroscopy (XPS). In this study, for the first time Co substrate was coated using fluoroalkylsilanes.

2. Experimental

2.1. Sample preparation

Silicon pieces were cut from a commercial p-type Si wafer (Cemat Silicon S.A.) and cleaned using ethyl alcohol, de-ionized water and dry argon (Ar) gas. Polycrystalline cobalt films with the thickness of 100 nm were deposited on oxidized Si(1 0 0) substrates, using the process of thermal evaporation at an incidence angle of 0° (with respect to the surface normal direction) in a system maintained at a base

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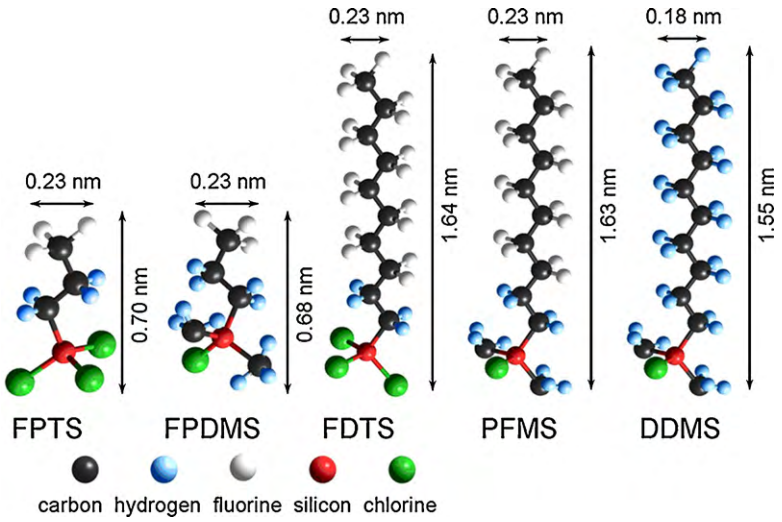

Fig. 1. Chemical structure of various fluoroalkylsilanes deposited on Co substrate.

pressure of about 10^{-5} mbar. The film thickness was determined by a quartz crystal microbalance. The next preparation step was the use of oxygen plasma to activate the surface before modification by fluoroorganic compounds.

2.2. Modification procedure

Deposition process parameters were optimized to produce the most hydrophobic surface possible. Static contact angle was measured to determine the degree of the hydrophobicity. Based on the measured contact angle, optimum deposition conditions were selected [19]. The cobalt surface activated by oxygen plasma was placed into a vapor phase deposition system and kept under low pressure (0.1 Pa). Then the specimen was kept in the modifier vapor for 20 min at room temperature and finally outgassed at low pressure for 1 h at 40 °C to remove any of physisorbed and unreacted molecules [20,21]. The samples were removed from the vacuum chamber and transferred into a vacuum desiccator until characterization.

The modification of the Co substrates was performed with five kinds of fluoroalkylsilanes precursors (Fig. 1): 1H, 1H, 2H, 2H perfluorodecyltrichlorosilane (FDTS), 1H, 1H, 2H, 2H perfluorodecyldimethylchlorosilane (PFMS), n-decyldimethylchlorosilane (DDMS), (3, 3, 3 trifluoropropyl)trichlorosilane (FPTS) and (3, 3, 3 trifluoropropyl)dimethylchlorosilane (FPDMS). These chemicals were chosen to compare the effect of chemical structure on tribological performance at the micro- and nanoscale. The effects of reduced bonding at the surface, carbon chain length, as well as the number of fluoride atoms in the chain were investigated. All precursors were ordered from the ABCR, GmbH & Co. KG, Karlsruhe.

2.3. Measurement techniques

2.3.1. Contact angle and surface free energy measurements

Static contact angles (SCAs) were measured in air by use of a sessile-drop method using a contact angle goniometer. A drop of proper liquid (water, glycerine and diiodomethane) was deposited on the substrate with the use of microsyringe. The image of the droplet was obtained by a digital camera. Images obtained were analyzed using Motic 2.0 software. All measurements were performed at (45 ± 5%) relative humidity and (22 ± 2) °C. The surface free energies of Co and surfaces modified by fluoroalkylsilanes were calculated using the Van Oss–Chaudhury–Good method [22].

2.3.2. Nanotribological characterization

The adhesion and friction measurements were performed with an AFM apparatus (Solver P47, NT-MDT) operating in air under ambient conditions. Nanotribological measurements were performed using a rectangular Si_3N_4 cantilever with a spring constant calibrated by the Sader method (k = 0.62 N/m) [23,24]. The adhesive force was obtained from the force–distance curve after reckoning the pull-off force [25–27]. The friction force was calibrated using the method described by Ruan and Bhushan [28]. The coefficient of friction was obtained from the slope of the friction force versus normal force plots. Applied loads typically ranged from 5 to 100 nN. The mentioned plots were linear in the investigated range of applied load. Friction force measurements were performed at a scan rate of 1 Hz and a scan size of 1 μm × 1 μm. Each measurement was repeated three times on different places of the sample surface. The obtained values of coefficient of friction were comparable. The average data are presented.

2.3.3. Microtribometer measurements

To compare the AFM and microtribological investigations, the samples were frictionally tested on a reciprocating ball-on-flat microtribometer, constructed in the Department of Chemical Technology and Environmental Protection, University of Łódź, Poland [21,29]. The microtribometer was operating in ambient conditions (relative humidity 45 ± 5% and temperature 22 ± 2 °C). Measurements were performed with the use of silicon nitride sphere (Si_3N_4) with diameter of 5 mm over a normal force range from 30 to 80 mN. The ball moved parallel with respect to the sample surface with velocity of 0.42 mm/s and the traveling distance of 5 mm. Each series of measurements were repeated three times in three different locations of the sample surface. The adhesive force was calculated from the negative horizontal intercept of the friction force versus applied load curve (the negative applied load value where the friction force is zero) [30]. The average data are presented.

2.3.4. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy was carried out using Omicron UHV system working at the base pressure lower than 5×10^{-8} Pa, equipped with the EA 125 HR hemispherical analyzer with the resolution better than 0.8 eV. The XPS investigations were carried out using Mg $K\alpha_{1,2}$ line with the power set at 75 W in all experiments. The two-point correction of the energy scale based on Au $4f_{7/2}$ (83.95 eV) and Ag $3d_{5/2}$ (368.22 eV) lines was applied to all spectra [31]. The XPSPEAK package was used to perform the quantitative analysis.

3. Results and discussion

3.1. Contact angle and surface free energy studies

Fig. 1 shows the chemical structure of five types of SAMs used in this study. The thicknesses of layers determined from the ellipsometric measurements on the cobalt surface modified by different compounds are comparable with the values obtained by the theoretical model determined using HyperChem 7.5 (Fig. 1). For FDTS, PFMS, FPDMS, FPTS and DDMS, they were found to be 1.95, 1.8, 0.71, 1.27 and 1.68 nm, respectively. These molecules were composed of vertical stacked chains in the trans–conformation of the close packed ~4.5–5 groups/nm^2 [32]. The thickness of FPTS layer on the cobalt surface is much larger than the theoretical value. This is probably due to vertical polymerization and formation of multilayers and agglomerates of the FPTS compound as well as ellipsometry measurement error (it could be up to ±0.5 nm).

Water contact angle and surface energy were measured to quantify the surface hydrophobicity and these results are compared in Fig. 2. All the fluoroalkylsilanes deposited on Co substrate increased the water contact angle, implying a higher surface hydrophobicity and directly proving the presence of the modifier on the surface. The compounds with fluorocarbon terminal group and backbone chain show a higher contact angle and lower surface free energy than methyl groups. Molecules with