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Tribological Behavior of Mono- and Multilayer Coverings on Silicon Surface

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Langmuir-Blodgett mono- and multilayer films from 2,4-heneicosanedione have been examined as lubrication coatings in the process of wear. Tribological properties of the films have been studied by atomic force microscopy and microtribometer. It has been observed that the wear resistance of silicon surface coated with OTS/LB multilayer system increased by several orders of magnitude compared to uncoated surfaces at low normal load. The results obtained suggest that the system constructed on silicon surface reduces surface energy, friction coefficient and increases life of substrate due to a possibility of LB film self-repairing during frictional contact.

Keywords: Langmuir-Blodget films, lubrication and adhesive coatings, AFM, tribology

1. INTRODUCTION

Adhesion interaction between monolayer films and solid substrates is of crucial importance in the field of boundary lubricants [1]. Chemical structure and composition of a film are critical as they ensure the film strength, frictional properties, uniformity and adhesion to the substrate [2]. Langmuir-Blodgett (LB) mono- and multilayer films may be used as protective and (or) lubricating molecular coatings depending on the nature of polar head and alkyl tail length. Nature and properties of surface should be also taken into account. The goal of this work is to construct mono- and multilayer LB covering on a modified silicon surface to improve its stability against wear.

2. EXPERIMENTAL PART

2.1 Materials

Octadecyltrichlorsilane (OTS) was purchased from Aldrich and used as received. 2,4-Heneicosanedione (HD, Fig. 1) was synthesized in accordance with [3]. Its copper complex, ($(HD)_2Cu$, Fig. 1) was obtained either via extraction reaction of Cu^{2+} ions (from cooper(II) chloride dihydrate) with HD or by reaction between HD molecules and Cu^{2+} ions at ionic subphase. Monolayers were spread from chloroform solutions on the surface of doubly distilled water (pH 5.3-5.5) or aqueous solution of $CuCl_2$ (0.5 mM). Y-type bilayers were transferred to the substrate by the traditional vertical deposition method. Z-type monolayers were also formed by the "horizontal precipitation" (HP) method [4]. The surface pressure during the deposition was kept at 30 mN/m.

Plates from silicon wafer <100> orientation were hydrophilized by heating in $H_2O:NH_4OH:H_2O_2$ mixture (7:4:1, in volume) at 320 K to clean a surface and to make it negatively charged. Such hydrophilic surface was either used for modification with LB film or hydrophobized with OTS in hexadecan:CCl_4 solution.

2.2 Instrumentation

An automated computerized Langmuir trough was used for measurements of surface pressure-area per molecule (π-A) isotherms and film deposition [4]. The isotherms were recorded at a compression speed of 0.2-0.3 $Å^2$/(molecule×min). AFM images were obtained with a Nanoscope IIIa (Digital Instruments, USA) operated in the constant force mode (1-10 nN). Tribological properties of samples were studied with microtribometer [5].

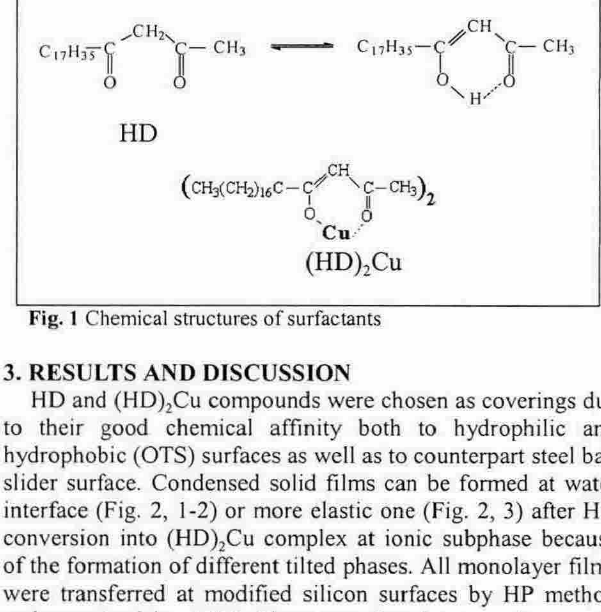

Fig. 1 Chemical structures of surfactants

3. RESULTS AND DISCUSSION

HD and $(HD)_2Cu$ compounds were chosen as coverings due to their good chemical affinity both to hydrophilic and hydrophobic (OTS) surfaces as well as to counterpart steel ball slider surface. Condensed solid films can be formed at water interface (Fig. 2, 1-2) or more elastic one (Fig. 2, 3) after HD conversion into $(HD)_2Cu$ complex at ionic subphase because of the formation of different tilted phases. All monolayer films were transferred at modified silicon surfaces by HP method and examined by AFM. There was found extremely smooth film surface for HD and $(HD)_2Cu$ monolayer on hydrophilic surface and a little bit disordered for HD and amorphous for $(HD)_2Cu$ (with numerous porous defects) on $Si/SiO_2/OTS$ surface. On the contrary, the best quality of a film was observed in the case of multilayer $(HD)_2Cu$ film transferred on hydrophobic silicon plate by vertical method. Thus, namely $(HD)_2Cu$ molecules inclined for bilayer structure's formation.

Adhesion of monolayer films to the silicon surface was estimated via force that should be applied during scanning to remove the material of monolayer from the surface. It was found strong resistance of HD monolayer to AFM tip influence. It was impossible to make a hole into HD monolayer on hydrophobic surface by standard oxide-sharpened Si_3N_4 integral AFM tips.

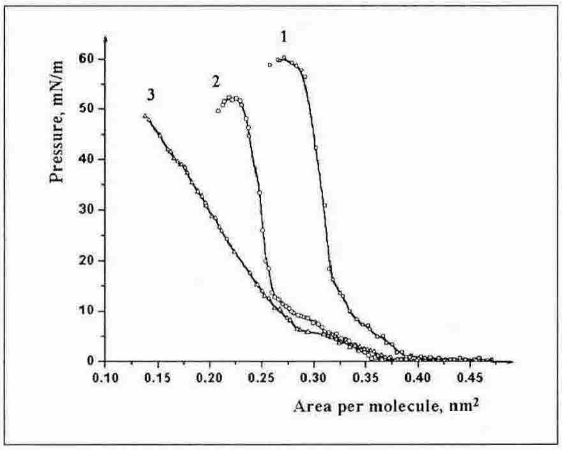

Fig. 2 π-A isotherms for (1,2) HD and (3) for $(HD)_2Cu$ recorded on aqueous (1, 2) interface and (3) ionic subphase.

Monolayer films also showed high stability on hydrophilic surface, though the holes were formed at ~10 nN of normal load (Fig. 3). $(HD)_2Cu$ monolayer was more stable on negatively charged surface and HD monolayer, on the contrary, on Si surface recharged with metal ions. That suggest about strong interaction of polar heads with silicon surface. At the same time, multilayer $(HD)_2Cu$ film was essentially more labile and can be displaced on surface with easily.

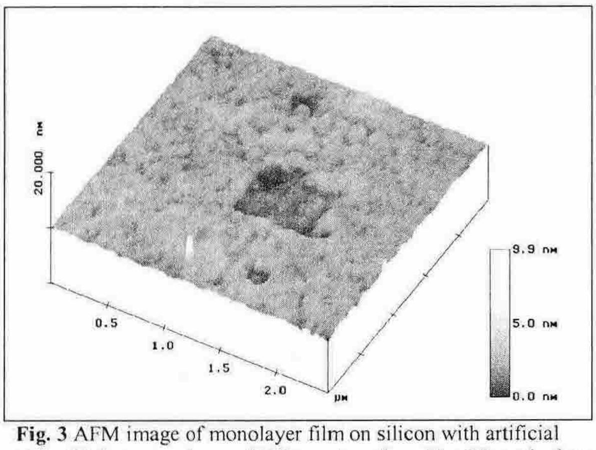

Fig. 3 AFM image of monolayer film on silicon with artificial scratched holes; monolayer of HD was transferred by HP method on hydrophilic surface.

Mono- and multilayer systems were also built on hydrophobized silicon wafers for wear testing by microtribometer. It was shown that OTS monolayer was much more mechanically stable over natural SiO_2 film on Si and showed reduced friction coefficient, Fig. 4, a-b. Moreover, OTS monolayer possessed not only enhanced long-term wear resistance but had good adhesivity to $(HD)_2Cu$ film. The data of Fig. 4c suggest that $Si/SiO_2/OTS/LB$ multilayer system was stable and resisted to steel ball slider influence during long period of time. Hence, OTS monolayer obviously prevents dewetting phenomena of amphiphilic molecules from LB film.

4. ACKNOWLEDGEMENT

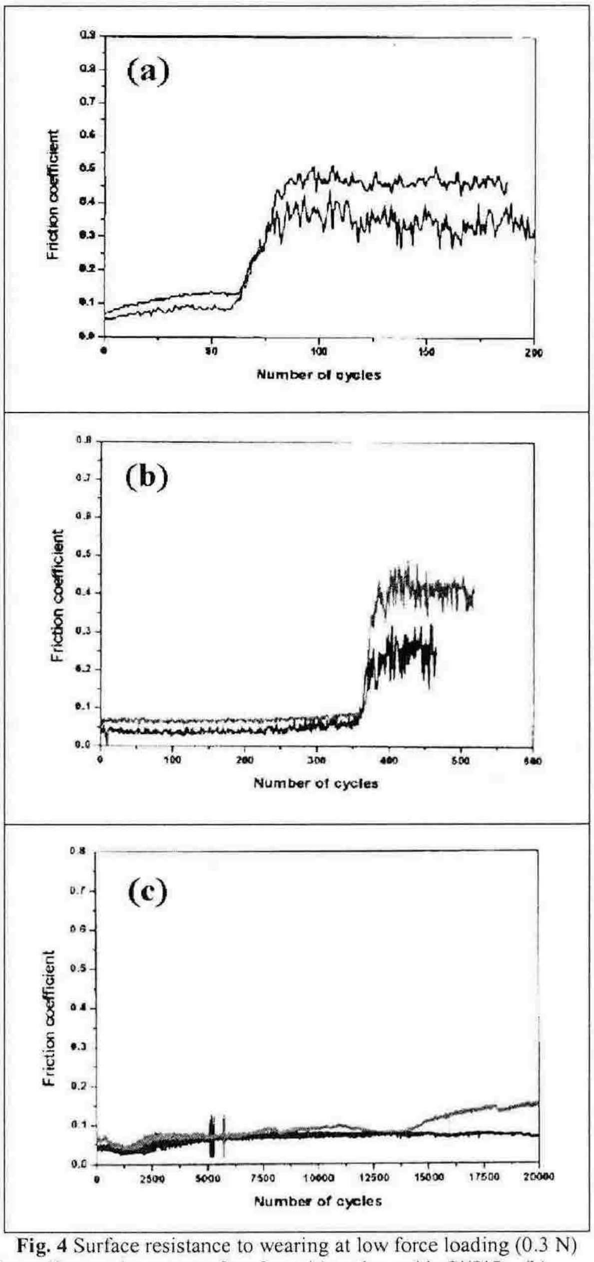

Fig. 4 Surface resistance to wearing at low force loading (0.3 N) depending on the nature of surface: (a) native oxide Si/SiO_2, (b) $Si/SiO_2/OTS$, (c) $Si/SiO_2/OTS$+50 bilayers of $(HD)_2Cu$.

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5. REFERENCES

[1] Micro/Nanotribology and its Applications, Ed. B.Bhushan, Klewer, Dordrecht, The Netherlands, 1997.
[2] Tsukruk, V.V., Adv. Mater., Vol.13, No.2, pp.95-108, 2001.
[3] Chaney, A., Astle, M.J., J.Org.Chem., Vol.16, No 1, pp.57-63, 1951.
[4] Agabekov, V.E., Zhavnerko, G.K., Staroverov, V.S., Bar, G., and Cantow, H.-J., Acta Physica Polonica A, Vol.93, No. 2, pp.383-386.
[5] H.-S. Ahn, C.-H. Kim, S.A. Chizhik, O.Y. Komkov, and A.M. Dubravin, Fine Friction and Wear Testing Apparatus, USA Patent pending (09/853,763), 2001.