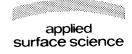


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Characterisation and stability of hydrophobic surfaces in water

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Abstract

The stability of four different hydrophobic surfaces in contact with water is assessed and discussed: H-terminated silicon, hexamethyldisilazane (HMDS) coated silicon, silicon surfaces covered with self-assembled monolayers (SAMs) of octadecyltrichlorosilane (OTS) and gold surfaces modified with SAMs of alkanethiols. Changes in hydrophobicity and surface oxidation were determined by contact angle measurements, X-ray photoelectron spectroscopy and AFM.

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1. Introduction

The preparation of homogeneous and molecularly flat stable hydrophobic surfaces plays an important role in technological applications, but is also of interest in studies of the dynamical and structural aspects of the solid/liquid interface. The interaction between solid surfaces separated by a thin layer of water is a central issue in many technological fields such as the study of friction and wear, and lubrication in an humid environment. Many experimental efforts have been made to measure the forces between hydrophobic surfaces in water by surface force apparatus and atomic force microscopes [1]. One

important conclusion derived in review by Christenson and Claesson [1] is that a number of controversial results have been generated due to changes in the surfaces properties during the experiments and due to a lack of characterisation before, during, and after the experiments. Indeed, it was found that surface forces between more robust and stable hydrophobic surfaces had a significant shorter range with respect to less stable surfaces [2,3].

Interfaces between water and hydrophobic surfaces have been widely studied in the last decades also in view of the fundamental role in molecular self-assembly processes governing the behaviour of biological membranes, micellar formation, and the stability of supramolecular structures. The properties of a liquid in the bulk differs quite markedly from the properties of the same liquid in the vicinity of a solid surface. The attractive/repulsive interactions between water molecules and the wall as well as the

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geometrical constraints induce structural rearrangements that extend over several molecular layers in the bulk liquid. These structural changes are reflected in the hydration forces between the two surfaces immersed in the fluid. Among the few methods available to probe experimentally such a thin interfacial liquid layer are neutron and X-ray reflectometry. However, both methods require long acquisition times, up to several hours in the case of neutron reflectometry. During this time, the surface must be stable, otherwise the results are questionable. Furthermore, surface roughness tends to increase the noise in the reflectivity curves, thereby limiting the observable range of momentum transfer [4] and consequently the resolution of the experiment [5]. It is therefore advisable to perform reflectivity measurements with surfaces as flat as possible. In addition, theoretical studies showed that hydrophobic hydration depends significantly on the radius of curvature of the hydrophobic body [6,7]. While water molecules can rearrange around small apolar molecules in order to maintain the network of hydrogen bonds, large objects tend to disrupt this network, thus affecting the density of water molecules in their vicinity. For flat surfaces, this means that the character of surface roughness in terms of corrugation and waviness will affect the hydration at the water/solid interface and care must be taken when results of different experiments are discussed and compared with each other.

In this work, four commonly used hydrophobic surfaces have been characterised in terms of their hydrophobicity, stability in water and surface roughness by means of contact angle measurements, X-ray photoelectron spectroscopy (XPS), and atomic force microscopy, thus exploring their potential use for the study of interfacial water layers.

2. Experimental

2.1. Chemicals and materials

Dodecanethiol (DDT, 98%+), hexamethyldisilazane (HMDS), octadecyltrichlorosilane (OTS, 90%+) were purchased from Sigma–Aldrich and used without further purification. Also ethanol, methanol, chloroform, dimethylformamide (DMF), hydrogen peroxide

 (H_2O_2) , concentrated sulfuric acid (all analytical grade) were used as received. Toluene absolute $(H_2O < 0.005\%)$ was purchased from Fluka. The water used was Baker HPLC analysed purchased from J.T. Baker. (1 0 0)-Silicon substrates were purchased from Crystec GmbH, Germany.

2.2. Surface modification

2.2.1. Silicon oxide hydrogenised by HF etching

New (1 0 0)-silicon wafers were first immersed in piranha solution (1/3 hydrogen peroxide + 2/3 sulfuric acid) for 10 min, and then immersed in 0.5% hydrofluoric acid for 10 min in order to remove the oxidation layer and replace it with a hydrogen termination. The HF etching was performed in precleaned plastic containers (sonication in a 3% aqueous solution of Decon 90 detergent, and rinsed with copious amount of Baker HPLC analysed water) since glass-ware is attacked by HF and could not be used. The samples were blown dry and stored under nitrogen for a maximum time of few hours before exposure to water. The measurement of contact angle and XPS were performed immediately after the samples were removed from water and blown dry with nitrogen.

2.2.2. Silicon oxide modified with hexamethyldisilazane

New (1 0 0)-silicon wafers were precleaned in piranha solution for 10 min, and sonicated with methanol, mixtures of methanol and chloroform and pure chloroform. Subsequently, they were placed under nitrogen and HMDS vapour overnight and cleaned in an ultrasonic bath in mixtures of chloroform and methanol.

2.2.3. Self-assembled monolayer of octadecyltrichlorosilane on silicon

New Si wafers (1 0 0) were immersed for 30 min in piranha solution, then rinsed with millipore water and ethanol. Subsequently, they were placed for 30 min in vacuum. Then the incubating solution, prepared with OTS in toluene at a concentration of 25 μM , was introduced under nitrogen overpressure, and left for 5 days. The samples were then placed in an ultrasonic bath of toluene and ethanol and blown dry with and stored under nitrogen.

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