

## Investigation of 3-mercaptopropyltrimethoxysilane self-assembled monolayers on Au(111) surface

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Received in revised form 5 August 2004; accepted 5 August 2004

Available online 25 September 2004

### Abstract

In this paper, preparation method of two-dimensional (2D) silica-like surface from self-assembled monolayers (SAMs) of 3-mercaptopropyltrimethoxysilane (MPTMS) on Au(111) surface is presented. The surface structure and morphology were characterized by scanning tunneling microscopy (STM) and secondary ion mass spectrometry (SIMS). In a first step, gold surface was imaged in order to find the topography. Then investigations were focused on MPTMS deposited on Au(111). Further steps like hydrolysis and condensation of MPTMS end-groups were performed and monitored by STM and SIMS methods. Hydrolysis and condensation reactions lead to 2D SiO<sub>2</sub> network called glass monolayer. It can be also described as 2D sol–gel processes. All procedures were performed in monolayer. When the state of end groups of MPTMS changes, i.e. when methoxy (Si–OCH<sub>3</sub>) groups undergo hydrolysis to silanols (Si–OH) groups, the surface topography changes. The similar phenomena may be observed when silanols undergo condensation and siloxy (Si–O–Si) bonds are created.

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**Keywords:** STM; ToF-SIMS; SAMs; 3-Mercaptopropyltrimethoxysilane

### 1. Introduction

The surface of different objects may be changed by deposition of diverse external layers. The thickness of these layers may be positioned in different scale range

and go down to few nanometers. In this case, the film thickness is very often equal to the thickness of monolayer. There are many kinds of monolayer preparation. One of the well-known methods is creation of self-assembled monolayers (SAMs).

Formation of crystalline monolayer of organic molecules on different solids, especially well-defined metal surfaces, is in the center of interest of many scientific communities. One of the most frequently

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studied system is formation of alkanethiols SAMs system on Au(111) surface. Such layers may play important role as a dense, thin (monomolecular) coating used as corrosion protection, microcontact systems, in biology with special multifunctional end-groups, and many others. Self-assembled monolayers may find also application in microcontact printing UV-lithography, e-beam writing [1]. ProFOUND studies of SAMs for advanced application in biology were presented in ref. [2]. It appears that SAMs modified with suitable chemical groups provide excellent system for the investigation of the interactions of proteins and cells with surfaces and biosurfaces.

Applications of SAMs are very vast: fabrication of novel molecular microstructures, biological sensing, studies of wettability, adhesion. The surface may be hydrophilic or hydrophobic depending on whether the terminal group is polar or non-polar. Besides the thiol on gold, thiols on silver surface are also known, however more difficult to prepare. Another family of SAMs are films formed by the adsorption of alkylsilanes onto silica. Such films exhibit high resistibility for oxidation and chemical attack.

SAMs are also in the field of interest of electro-analytical applications. Mirsky in his paper [3] presents some aspects of self-assembly like exploitation of electrical control of self-assembly of thiol compounds for electrically-addressable immobilization of receptor molecules onto sensor arrays, a spread-bar technique for formation of stable monostructures and use of self-assembled monolayers as selective filters for chemical sensors.

Structural analysis of alkanethiols on Au(111) is one of the main aim of the scientific research. Alkanethiols molecules on gold surface may be arranged in hexagonal system ( $\sqrt{3} \times \sqrt{3}$ )R30° or ( $p \times \sqrt{3}$ ) structures. Other arrangements were also reported. Some of the authors investigated also alkenethiols SAMs with different length of alkyl chain in order to explain its influence on organization on the surface. They postulated creation of sulphur dimmers on Au(111) surface [4]. Decanethiol monolayers self-assembled on Au(111) can be also created by molecular beam deposition [5]. Toerker et al. [6] reported different possibilities of thiol organization. Structural changes may be followed by varying the exposure in gas phase deposition, in situ scanning tunneling microscopy

(STM) imaging in very dilute decanethiol solution or annealing of densely-packed films.

The kinetics mechanism of self-organization on Au(111) was investigated from the electrochemical point of view by Rohwerder et al. [7]. It was found that the self-assembly of thiol molecules deposited from ethanol solution on Au(111) depends on electrode potential. At cathodic potential, the thiol molecules adsorb flat on the surface. On more polarized surfaces like iron surface (more reactive surface), the thiol molecules crack and the created monolayer is not stable.

The stability of thiol SAMs on gold was investigated by Chung et al. [8] by FT-IR external reflection spectroscopy. Self-exchange of thiols molecules was monitored by C–H and C–D stretching vibration modes for deuterated and undeuterated alkanethiols by FT-IR.

Self-assembled monolayers allow the study of a vast number of reactions on surfaces finding different applications like cell-binding or self-cleaning surfaces. Vast numbers of two-dimensional (2D) chemistry examples, including many types of chemical reactions taking place at the ends of molecules in SAMs are presented in refs. [9,10]. Besides reports of decanethiol SAMs on Au(111), also more complex systems like SAMs with terminal reactive end-groups are investigated. Among them especially 3-mercaptopropyltrimethoxysilane (MPTMS) is the object of many studies.

Cabrera et al. [11] reported a new method for controlling electrochemically, the defect sites in SAMs. In this manner, nanosized molecular recognition system can be created.

In another experiment, the same author [12] demonstrated the adsorption of MPTMS on iodine-coated gold electrode in order to create lower density monolayer than the monolayer of MPTMS over pure gold.

Hu et al. [13] reported self-assembled MPTMS layers on silicon oxide SiO<sub>2</sub> prepared at different MPTMS concentrations. It was found that the structure and morphology of MPTMS layers depend on MPTMS concentration and are composed of dispersed domains rather than continuous and flat monolayers.

MPTMS was also used as linker molecule. Chau et al. [14] present novel strategy to prepare colloidal Au multilayers, i.e. nanostructure which consists of alternate layers of ultrathin thiol-functionalised silica films and Au colloids.

Another types of molecules, being also thiols but carrying acid group, was also in the field of interest from the point of view of their structural assembly on the surface. Sawaguchi et al. [15,16] studied structural properties of 3-mercaptopropionic acid and mixed system of 3-mercaptopropionic acid and 1-decanethiol on Au(111).

Many surface analytical methods have been employed to characterize SAMs. First of all scanning tunneling microscopy has been used in order to determine the two-dimensional ordered structure of SAMs on conductive surfaces. Among other methods especially helpful have been diffraction methods, near edge X-ray absorption fine structure (NEXAFS), surface extended X-ray absorption fine structure (EXAFS). Both methods serve to characterize bonding properties between SAMs and substrate. Other methods like XPS are difficult to interpret because of the weakness of the signal coming from sulphur. Another method, which however is not used very often, is secondary ion mass spectrometry (SIMS). The difficulty of this method is that SAMs built mainly of sulphur and long alkyl chains do not generate easily fragmented ion peaks because of the cross-linking between adsorbates. But for SAMs carrying on their terminal atoms reactive (or even not reactive) end groups, SIMS appears to be quite helpful in monitoring reactions taking place on the surface. More details about the SIMS technique are presented in refs. [17–21].

In this paper, preparation method of molecularly smooth 2D silica-like surface from 3-mercaptopropyltrimethoxysilane on Au(111) is presented. The deposition conditions as well as hydrolysis and condensation reactions in monolayer leading to model SiO<sub>2</sub> surface creation are elaborated.

## 2. Experimental

### 2.1. Samples

In our experiment, the following samples were investigated:

- (a) Au(111) deposited on mica;
- (b) 3-mercaptopropyltrimethoxysilane and its derivatives.

### 2.2. Samples preparation

#### 2.2.1. Gold—Au(111)

In order to exploit well-defined surface, which fulfils special requirements like chemical stability, high conductivity and ease to handle and process, gold was chosen as support solid. Additionally, gold surface is atomically flat what assures defined deposition conditions. Stable thiols SAMs can be achieved on gold surfaces because of their property to chemically bond sulphur. In our experiment, gold deposited on mica was used. The crystal parameters of mica are close to the gold crystal parameters, so mica is suitable support for gold deposition. Details about Au(111) surface preparation are presented in ref. [22]. Gold solid support was used as achieved in STM imaging without any preliminary treatment.

#### 2.2.2. Preparation, hydrolysis and condensation of 3-mercaptopropyltrimethoxysilane on gold

Solution of 3-mercaptopropyltrimethoxysilane in ethanol was prepared at concentration  $\sim 10^{-4}$  mol/L. Gold sample was immersed in solution for 0.5 h and washed in water and ethanol, purged in argon flow and annealed at 60 °C for 12 h. In order to carry out hydrolysis reaction of terminal methoxy-end groups, deposited film was hydrolyzed in 0.01 mol/L HCl solution for 15 min and dried in argon flow. Condensation reaction was carried out in air at 60 °C during 12 h.

### 2.3. Chemical

3-Mercaptopropyltrimethoxysilane was used as achieved without any pretreatment (ABCR, 97%). Gold—GA PVD-Beschichtungen, Heidelberg. Ethanol—Eurochem BGD Ltd. —99.8%.

### 2.4. STM instrumentation

STM measurements were performed with the use of commercial AFM/STM system (Solver P47, NT-MDT) operating as STM in ambient conditions. Typically images were acquired in constant current mode with bias voltage of about 0.3 V and with tunneling current 0.2 nA. Some high resolution images were acquired in constant height mode. STM tips were prepared by cutting Pt/Ir (80:20) wires with 0.5 mm

diameter. Sample surfaces were scanned in different places with area ranging from several microns down to few nanometers.

### 2.5. SIMS instrumentation

The secondary ions mass spectra were recorded by a time-of-flight (ToF)-SIMS IV mass spectrometer manufactured by Ion-ToF GmbH, Muenster, Germany. The instrument is equipped with liquid metal  $^{69}\text{Ga}^+$  primary ion gun and high mass resolution time-of-flight mass analyzer. During an analysis, an  $40\text{ }\mu\text{m} \times 40\text{ }\mu\text{m}$  area of the sample surface was irradiated with the pulses of 25 keV ions at 10 kHz repetition rate and an average ion current 2.5 pA. The analysis time was 20 s giving an ion dose of approximately  $2 \times 10^{13}$  ions/cm<sup>2</sup>. Secondary ions emitted from the bombarded surface are mass separated and counted in time-of-flight analyzer. Positive secondary ions mass spectra were recorded with high mass resolution typically greater than 5900 at the 29 m.u. with the primary ion pulse width 650 ns.

## 3. Results and discussion

### 3.1. STM measurements

#### 3.1.1. Gold

In Fig. 1, the surface of Au(111) is presented. The surface is smooth with atomic size features. The gold surfaces exhibit atomic steps and terraces which correspond to monoatomic interlayer distance, i.e.  $\sim 0.29$  nm for gold.

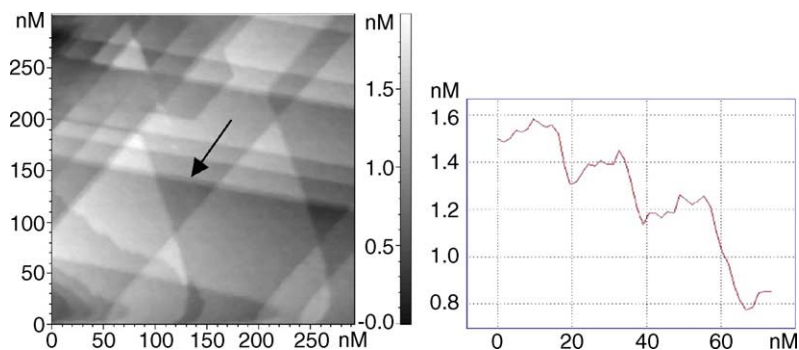


Fig. 1. STM images of gold—Au(111).

#### 3.1.2. 3-Mercaptopropyltrimethoxysilane (MPTMS) on gold

In Fig. 2, the gold surface with MPTMS is presented. In molecular resolution range, stripped-like structure is very well visible. It is known that the behavior of MPTMS on gold surface and their organization structure are influenced by following forces: (i) interactions between thiols head groups and Au lattice; (ii) interactions between alkyl chains having dispersion character; and (iii) interactions between end groups of thiols. Final molecular organization and specific topography are the result of the balance between these three forces [23]. When one compares the two systems, e.g. alkanethiol on Au(111) versus MPTMS on Au(111), it is clear that interactions mentioned above are not the same in both cases.

Although one can assume that interactions between thiol head group and gold surface would be the same in both cases, the remaining two interactions are different. The main difference is that MPTMS have bigger end-group and shorter hydrocarbon chain. As a consequence, the interactions between hydrocarbon chains for MPTMS are very weak and additionally screened by large end group. Therefore, the main factor which governs the final structure of MPTMS on gold, observed by STM is the presence of end groups. When we analyze the cross-section of the STM image of MPTMS on gold one can measure that the distance between the maximum values of peaks is between 1.2 and 1.5 nm. When the width of the peak is analyzed, it corresponds to the distance of around 0.5–0.7 nm. We found from computer simulation (HyperChem software), which was used to calculate

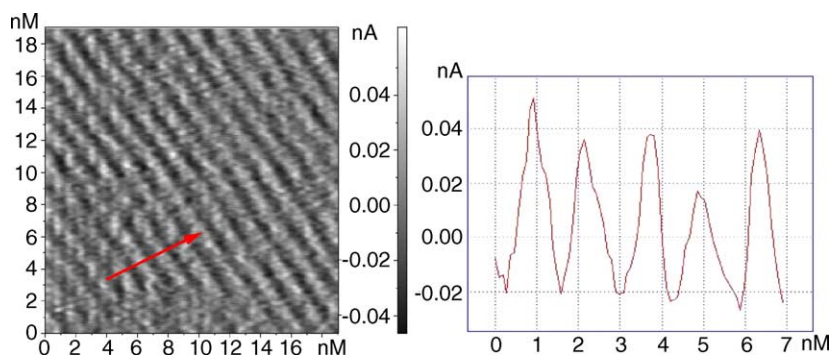


Fig. 2. STM image of 3-mercaptopropyltrimethoxysilane on Au(111) surface.

the size of MPTMS molecule, that the maximum dimension was 0.6–0.7 nm. It corresponds very well with the width of the stripe measured by STM. The above considerations indicate that MPTMS molecules are arranged in the form of long rows where molecules follow one by one, what is visible in the STM image as separate long stripes. Reactive end groups open the possibility of further applications in preparation of covalent multilayer films. These films can be created by attaching different groups to the end groups of molecules. This kind of research is planned to be done in the future. Here, we focus on the reaction of hydrolysis and condensation taking place between thiols end groups (Fig. 3).

The reaction of hydrolysis and condensation of metal alkoxides is well-known in macroscopic scale and called sol–gel chemistry [24]. In our experiment, we use the same reaction but in monolayer. In contrary to STM images of as-deposited MPTMS sample, where well visible stripped-like structure was detected, STM images of MPTMS after hydrolysis and condensation do not exhibit any ordered features (not shown). It may be assigned to the creation of silica-like 2D surface which is amorphous and causes disappearing of the stripped structure. There are two

reasons of this phenomenon: (a) thiols may migrate on gold surface when temperature increases; and (b) short alkyl chains reorganized parallel to the surface. These two factors make possible the Si–O–Si bond creation which typical distance is  $\sim 0.32$  nm.

Similar investigation of MPTMS on Ag and Au surfaces was reported by Pemberton and co-workers [25,26]. In contrary to our STM and SIMS studies especially Raman spectroscopy was used in order to detect the chemical state of deposited molecules. These measurements correspond very well with our SIMS results (described below). Cyclic voltammetry was used in order to investigate the defect structure of MPTMS monolayers. It is interesting that after surface reactions, on the basis of cyclic voltammetry results, authors postulate the existence of Si–O–Si network across the surface. It is in good agreement with our STM measurements. It was difficult to find any ordering in STM images of MPTMS after hydrolysis and condensation, because of the blocking and/or screening the current between tip and sample by created Si–O–Si network. Additionally, estimation of surface silanols coverage exhibited low level, what again was confirmed by our SIMS measurements where the level of surface silanol upon hydrolysis

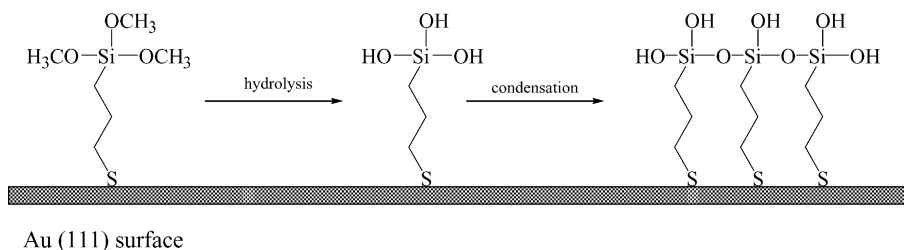


Fig. 3. Model of MPTMS reactions leading to 2D silica-like surface.

Table 1

ToF-SIMS positive secondary fragmentation ions analysis of 3-mercapto-propyltrimethoxysilane on gold: as-deposited, after hydrolysis and after condensation

	Fragmentation ions					
	SiOH (44.98 <sup>a</sup> )	Si(OH) <sub>2</sub> (61.98 <sup>a</sup> )	Si(OH) <sub>3</sub> (78.99 <sup>a</sup> )	SiOCH <sub>3</sub> (59.00 <sup>a</sup> )	Si(OCH <sub>3</sub> ) <sub>2</sub> (90.01 <sup>a</sup> )	Si(OCH <sub>3</sub> ) <sub>3</sub> (121.03 <sup>a</sup> )
As-deposited	131.9	5.2	–	515	68	478
After hydrolysis	430	12.5	53.3	25.6	3	–
After condensation	19.4	0.7	5.9	2.3	–	–

<sup>a</sup> Molecular mass.

initially increases but decreases rapidly after condensation.

### 3.2. SIMS measurements

Monolayers of 3-mercaptopropyltrimethoxysilane were characterized with ToF-SIMS spectrometry in order to establish the chemical state of reactive end groups. The number of counts for chosen fragmentation ions is presented in Table 1 (positive secondary ions).

From Table 1, it is clear that postulated hydrolysis reaction of 3-mercaptopropyltrimethoxysilane end groups took really place. First of all, an increase of the signal from SiOH and Si(OH)<sub>2</sub> groups is well visible. The level of these groups is not very high in the initial state of monolayer but during hydrolysis methoxy-groups are converted to SiOH groups and their number is increasing what is confirmed by the signal coming from Si(OH)<sub>n</sub> groups. Similarly, a decrease of the signal assigned to Si(OCH<sub>3</sub>)<sub>n</sub> groups is observed. These groups are present only in the initial state of MPTMS and are not present if hydrolysis reaction takes place.

The same experiment was performed for the sample submitted to condensation. It is expected that during condensation silanols will be converted to siloxy groups which connect neighbouring molecules. It is clear that drop of the intensity signal originating from SiOH, Si(OH)<sub>2</sub>, Si(OH)<sub>3</sub> and SiOCH<sub>3</sub> ions indicates the successful condensation process.

## 4. Conclusions

In this paper, self-assembled monolayers of 3-mercaptopropyltrimethoxysilane on Au(111) surface

as a preparation method of 2D silica-like surface was presented. Self-assembled monolayers structure and morphology have been studied using scanning tunneling microscopy and time-of-flight secondary ion mass spectrometry. The hydrolysis and condensation processes of MPTMS end-groups were performed in the monolayer. In this case, 2D silica-like network, called glass monolayer, was created. The conditions of thiols deposition were elaborated and the condition leading to the hydrolysis and condensation of deposited 3-mercaptopropyltrimethoxysilane layer on gold was found.

From studies presented in this paper, it can be concluded that 3-mercaptopropyltrimethoxysilane has self-assembling properties. Using this compound opens the possibility of building more complex layers by attaching next levels of molecules. In this way, multilayer structures may be obtained. Such structures may find application in tribological systems where the top layer play anti-frictional role and the bottom ones have anti-wear properties. Such structures and their nanotribological behavior are currently under study.

## Acknowledgement

This work was supported by the State Committee for Scientific Research (KBN) under Grant number 7 T08C 06320.

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