Chemical Physics 428 (2014) 105–110

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Highly-ordered self-assembled monolayer of alkanethiol on thermally annealed polycrystalline gold films

Young-Kyu Hong [1], Hyunung Yu *, Tae Geol Lee, Noah Lee, Jae Ho Bahng, Nam Woong Song, Won Chegal, Hyun Kyong Shon, Ja-Yong Koo *

Korea Research Institute of Standards and Science, P.O. Box 102, Yuseong, Daejeon 305-600, Republic of Korea

ARTICLE INFO

Article history:
Received 25 August 2013
In final form 28 October 2013
Available online 7 November 2013

Keywords:
Surface
Roughness
Self-assembled-monolayer
FT-IR
TOF-SIMS

ABSTRACT

We report a gold substrate manipulation from very-flat to highly-curved surfaces with a thermal treatment as a function of annealing temperature, which greatly affects the quality of SAM with respect to density and ordering. Annealing of gold film greatly removes nanometer-scale protrusions, leading to a very-flat surface with a large grain size as comparable with gold coating on mica. The quality of alkanethiol SAM are evaluated using Fourier transform infrared and time of flight secondary ion mass spectroscopy. Our proposed method delivers good ordering between molecules in the SAMs to promote a high density on extremely small areas for a cost-effective and miniaturized biochip.

1. Introduction

Self-assembled monolayer (SAM) of alkanethiols on metal has been extensively studied due to their wide applications, for example, from electronic devices such as light-emitting diodes, solar cells, or field-effect transistors to corrosion inhibition, surface patterning, wetting inhibition and biosensors [1–4]. The surface characteristics are critical to the properties of organic–inorganic interfaces. Surface treatment by formation of a self-assembled monolayer on a solid metal or oxide electrode can markedly improve the molecular order at the interface thus to improve the device characteristics via interface functionalization [1–5]. In particular, modification of a gold surface with alkanethiolate SAMs has been extensively studied. The strong chemisorption bonds of organosulfur compounds on a gold surface have attracted considerable attention that has led to many basic studies on dense and well-ordered self-assembled-monolayer [6–9]. Alkanethiolate SAMs terminated with various functional groups such as OH, NH_2, COOH, $CH=CH_2$, $C{\equiv}CH$, Cl, Br, CN, $Si(OCH_3)$, $CONH_2$ are important for engineering of surface properties or for further chemical conjugation. In particular, OH and COOH terminals are most common and widely studied for their simplicity and flexibility as headgroups. Physical properties of SAMs with these terminals such as density, ordering, stability, and wettability are very important while immobilizing bio-molecules or connecting organic molecules between metallic electrodes with respect to reproducible and desired functional behaviors [10–15]. A miniaturized biochip composes of a patterned substrate to immobilize biomolecules on a high-density and good ordering of SAM. For a better performance, mixed SAMs are often utilized to control SAM coverage tunable for a designed surface charge, stability, wettability and biocompatiblility [6–8]. The spacers with different chain lengths – often CH_3 and OH terminals as hydrophobic and hydrophilic neutral species – are utilized to control the density of biomolecules in biochips and biosensors. The parameters of SAM formation such as immersions time, concentration of adsorbate, and chain length (structure of the adsorbate) on the structure and properties of SAMs are well-studied, but little has been studied on the substrates where SAMs are adsorbed.

For a formation of thiol-bound SAMs, a pre-cleaned substrate of noble metal is immersed into a dilute ($\mu M \sim mM$) ethanolic solution of thiolates. Gauche defects (chain disorder) are inevitable but can be reduced by increasing dipping time. Kinetic study of alkanethiol adsorption onto Au(1 1 1) surfaces shows that a well-aligned and dense coverage of adsorbates with little defects in the SAM is achieved with a reorganization process for several hours after a quick Langmuir adsorption [6–8]. Defects in SAMs also result from the surface variations of the polycrystalline gold substrate such as intergrain boundaries, faceting, occlusions, corrugation, and pebbly structure [6,7]. A large grain size of

* Corresponding authors. Tel.: +82 42 868 5786; fax: +82 42 868 5032 (H. Yu). Tel.: +82 42 868 5334; fax: +82 42 868 5047 (J.-Y. Koo).
E-mail addresses: peacewithu@kriss.re.kr (H. Yu), koojayon@kriss.re.kr (J.-Y. Koo).
[1] Present address: Korea Electronics Technology Institute(KETI), Jeonju, 561-844, Republic of Korea.

0301-0104/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.chemphys.2013.10.019

substrate can be achieved by a simple annealing process at an inert atmosphere to produce a nearly single-crystal and low step density gold surfaces up to a few micrometer domain [8]. This in turn collapses the irregular structures to remove defect contents, thereby to flatten the gold substrate for growing a close-packing high-ordered alkanethiolates SAMs [6,7]. For a very thin gold film, the surface rather fissures off each other to form a pebble structure by a surface tension during the annealing process. As a result, the gold nanoparticles with a coarse size distribution and the nanogap between gold agglomerates are randomly patterned on a SiO_2/Si wafer.

A quantitative analysis of the SAMs adsorbed on the gold surface is crucial for the evaluation of coverage. In this study, we discuss on the substrate control with respect to surface and crystallinity. First, surface roughness of gold substrate is investigated with an atomic force microscopy (AFM) and a field emission scanning electron microscopy (FE-SEM). Then, a Fourier transform infrared (FT-IR) and a time of flight secondary ion mass spectroscopy (ToF-SIMS) technique are applied to quantify the chemical composition of alkanethiol SAMs with characteristic bands of CH_2, CH_3 and COOH groups in mercaptoundecanoic acid and mercaptododecane.

The best quality alkanethiol SAMs are expected from the well-ordered ones formed on an atomically flat, single crystal gold surface [16]. However, for the practical applications using SAMs, there is a need for cheap, well-ordered, and reliable gold films formed on common silicon or glass wafers. Nonetheless, the surface of as-deposited gold on a silicon wafer has irregular corrugations with randomly oriented amorphous or small polycrystalline grains at a nanosized level [16,17], which may results in considerable disordering between the alkanethiol molecules in the SAM thereon [16,18–20]. We have found out a facile process to improve the ordering in the SAM on a patterned gold surface (Scheme), thus the reliability of SAM-applied devices would be significantly increased.

2. Experimental section

2.1. Substrate and monolayer preparation

First the 1 μm-thick SiO_2 film is grown on the commercially available silicon wafer to prevent a formation of gold silicide from various gold surfaces. Then, four types of gold film from most flat to highly curved surfaces – (1) very-flat gold on mica (2) annealed (3) as-deposited or non-annealed (4) highly-curved gold nanoparticles – are prepared on SiO_2 layer because the geometry of the gold surface is believed to be the primary factor for determining the ordering between the molecules in the SAM (Scheme). The preparation details on gold films are as follows. (1) The very flat gold film on mica is purchased from Molecular Imaging and simply cleaned with anhydrous ethanol. (2) The 100 nm-thick gold films on SiO_2/Si wafer by thermal evaporation are annealed at various temperatures (60, 90, 120, 150, 300, and 600 °C) for 30 min under 1 atm of Ar (50%) and H_2 (50%). (3) The as-deposited gold film without annealing is prepared by the usual procedure; the adhesion layer of 10 nm-thick Cr followed by 100 nm-thick gold is deposited on SiO_2/Si wafer. (4) The gold film with highly curved surfaces is prepared with self-agglomeration process. Annealing of very thin (4 nm-thick) gold layer on SiO_2/Si wafer at 600 °C for 30 min allows gold film fall apart to be isolated each other by a surface tension to form a pebble structure. The AFM and the FE-SEM (Phillips XL30S) are utilized to characterize the surface topography of the above Au samples before SAM formation.

For the SAM formation, 11-Mercaptoundecanoic acid [MUA, $HOOC(CH_2)_{10}SH$] and 1-dodecanethiol [DDT, $CH_3(CH_2)_{11}SH$] are purchased from Sigma Aldrich since these chemicals are most common and widely studied. Gold films are immersed in a 1 mM dehydrated ethanol solution of MUA and DDT at 25 °C for 12 h. This concentration and immersion time are quite enough for maximum coverage of *n*-alkanethiol molecules (7.6×10^{-10} mol/cm^2) since the value corresponds to the overlayer structure of alkanethiol adsorbed on Au(1 1 1) surfaces as determined by He diffraction [4,8]. Then, the samples are removed from the solution and rinsed with absolute ethanol to wash out unbound thiols molecules to remove the possible double layer via interplane hydrogen bonds of MUA [21] and dried in a nitrogen gas. A non-specific binding ratio of SAM between Au and Si surface is confirmed with a ToF-SIMS analysis to be below 0.001.

2.2. Surface characterization

For FT-IR analysis, reflection–absorption method is adopted using a FT-IR spectrometer (Nicolet 6700, Thermo Electron) with a polarized infrared external reflectance accessory. This instrument is operated at a grazing-angle specular reflectance and a MCT detector is used for a high sensitivity. The *p*-polarized light is incident at 80° relative to the surface normal. All the spectra are averaged after 128 scans at a resolution of 2 cm^{-1} with a stream of N_2 gas and referenced to a clean gold film. The IR spectral range between 2800 and 3000 cm^{-1} are chosen since this band is least interfered with the atmosphere such as H_2O and CO_2 for high reproducibility. The spectra are resolved into 7 Gaussian functions as shown in Fig. 2, of which main peak position and linewidth are summarized in Table 1 for MUA and in Table 2 for DDT, respectively.

ToF-SIMS measurements are performed by using a ToF-SIMS instrument (ION-ToF GmbH, Germany) equipped with a 25 keV Bi^+ ion gun. For ToF-SIMS imaging, the ion gun is operated at 10 kHz, and the average ion current measured using a Faraday cup is 1.0 pA (Bi^+) at the grounded sample holder. A pulse width of 0.7 ns from the bunching system resulted in mass resolution ($M/\Delta M$) of 7919 at m/z 197 (Au) in negative mode. An area of 500×500 μm^2 is rastered by primary ions and is charge compensated by low-energy electron flooding. The primary ion dose is kept at the same amount of 5.0×10^{12} ions/cm^2 to ensure static SIMS conditions. The negative ion spectra are internally calibrated by using CH^-, C_2H^-, C_3H^-, and Au^- peaks. SIMS images are taken in negative SIMS mode at 256×256 pixels with the spatial resolution of 5.0 μm.

3. Results and discussion

The AFM and the FE-SEM are adopted to characterize the surface of Au substrate for SAM formation. Fig. 1 presents a series of AFM images (1×1 μm) of gold films annealed at different temperatures. Apparently, surface roughness greatly decreases from that of as-deposited Au substrate as the annealing temperature is elevated. The pebbly surface of as-deposited film becomes flatter and the apparent size of the gold grains gets larger with varying levels of corrugation. There is no indication of island formation from the 100 nm-thick Au film revealing that the gold surfaces are still continuous. A degree of surface roughness or a curvature of surfaces (second spatial derivative) of as-deposited Au film is measured at 2.03 nm (root-mean-squared) from an AFM profile [17]. When an annealing temperature increases, these values decrease to 1.35, 1.23, 1.10, 1.06, and 0.88 nm at 60 °C (b), 90 °C (c), 120 °C (d), 150 °C (e), and 600 °C (f), respectively.

The FE-SEM image of as-deposited Au film also shows many irregular nanometer-scale protrusions on the surface. The annealing process at higher temperatures effectively removed the