Corrosion Behaviors Studied in Self-Assembled Processes of Alkanethiol Monolayers on Polycrystalline Gold Substrates

Z. CAO [1, a, ¶], Z.L. XIAO [1], N. GU [2, b], S. SHIMADA [3], T. FUKUDA [3]
and H. MATSUDA [3, c]

[1] Department of Chemistry and Environmental Engineering, Changsha University of Science and Technology, Changsha 410077, China

[2] Jiangsu Laboratory for Biomaterials and Devices, National Laboratory of Molecular and Biomolecular Electronics, Department of Biological Science and Medical Engineering, Southeast University, Nanjing 210096, China

[3] National Institute for Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305, Japan

[a]zhongcao04@yahoo.com.cn, [b]guning@seu.edu.cn, [c]hiro.matsuda@aist.go.jp

¶Corresponding author

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Abstract. In this paper, the corrosion phenomenon occurred on the polycrystalline gold substrates has been for the first time observed by *in situ* quartz crystal microbalance (QCM) method for adsorption of alkanethiol monolayers, which may be attributed to thiol-induced dissolution of gold during the adsorption process in the presence of oxygen. It is evident from the image of many corrosive defects or holes produced on the surface of gold grains by using atomic force microscopy (AFM). The kinetic equation on corrosion rate of gold dissolved in the organothiol solution has been obtained. The gold corrosion rate at fast stage can be estimated to be 9.2×10^{11} Au atoms cm^{-2} s^{-1}.

Introduction

Self-assembled monolayers (SAMs) of linear alkanethiols ($CH_3-(CH_2)_{n-1}-SH$) adsorbed onto Au substrates like single crystalline Au(111) or Au(111)/mica surfaces have been widely investigated due to their easily preparation, believable density, long term stability and high structural quality [1]. In particular, there were increased reports on the nature of holes or pits in self-assembled thiol monolayers which have been found frequently in scanning-tunneling microscopy (STM) studies [2, 3], that may be attributed to thiol-induced dissolution of gold during the adsorption process of thiol molecules. By atomic absorption spectroscopy of polycrystalline gold substrate, Edinger et al have firstly presented quantitative data for gold solubility in thiol solution in the presence of oxygen [4]. However, relatively few have monitored the gold corrosion accompanied in alkanethiol assembled processes on line. In the present paper, the corrosion phenomena occurred on the polycrystalline gold substrates have been for the first time observed by *in situ* microbalance method for adsorption of alkanethiol monolayers in oxygen saturated tetrahydrofuran (THF) solution, combining with atomic force microscopy (AFM) observations in the same time, that will guide people for further surface modification of bio-chips, chemical and bio-sensors, etc.

Experimental

Chemicals. Alkanethiols ($C_nH_{2n+1}SH$ for n=3-10, 11, 12, 16, and 18) were obtained from three sources (Sigma-Aldrich of USA, n=3, 5, 7, 9, 11, 18; Eastman Kodak of USA, n=4, 10, 12, 16; Wako of Japan, n=6, 8). The tetrahydrofuran (THF) solvent was freshly distilled prior to use. All other chemicals used through out the experiments were of reagent grade or better if not stated elsewhere.

Microbalance Device. A commercial measurement system of a quartz crystal microbalance (QCM) was obtained from USI Corporation, Japan, which consisted of quartz crystal oscillating circuit, temperature controller, and a universal counter (Model 53131A, Hewlett Packard Co., Japan).

An AT-cut QCM with a fundamental resonance frequency of 9 MHz (USI Co., Japan) was connected to the circuit and the counter. The QCM substrate was prepared by vacuum thermal evaporation (less than 5×10^{-5} Torr) of high-purity gold (2000 ~ 3000 Å) onto the surface of quartz crystal that had been pre-coated with chromium (100 Å) to improve adhesion. The gold substrate of QCM was polycrystalline by thus preparation. All QCM measurements were conducted at controlled temperature of 25 ± 0.1 °C.

Monolayer Preparation. For comparison, alkanethiolate monolayers were deposited by their spontaneous adsorption from air-exposed, nitrogen and oxygen-saturated THF solutions (4 ~ 400 × 10^{-6} M) on gold substrates of QCMs, respectively. The formation of n-alkanethiol monolayers were monitored by *in situ* QCM device with the immersion time. Upon removal from solution, the thiol-modified QCMs were thoroughly rinsed with pure THF, dried in a steam of pure N_2, and immediately imaged by a scanning probe of AFM.

Atomic Force Microscopy. All images were recorded in the contact mode by using a scanning probe microscopy (Nanoscope IIIa, Digital Instruments, Inc., Santa Barbara, CA). The cantilevers used were the silicon nitride probes with the pyramidal tips and the spring constant of 0.06 and 0.12 N/m. The piezo scanners in the AFM had a scan range of 14.1 μm × 14.1 μm × 2 μm and 1.2 μm × 1.2 μm × 0.7 μm, respectively.

Results and Discussion

Figures 1a and **1b** show two typical kinetic response curves of n-dodecanethiol self-assembled on the surfaces of polycrystalline gold grains of QCMs in nitrogen and oxygen saturated THF solutions, respectively, showing two kinds of response behaviours with distinct frequency-decreased (FD) and frequency-increased (FI) processes. For thiol SAM formation in natural air-exposed THF solution, the response behaviour included both FD and FI processes.

Usually, the fundamental frequencies of oscillating crystals (called as F_0) were very stable in the gas like nitrogen or oxygen saturated THF solvent, whose standard deviation was less than ± 0.3 Hz. After an appropriate amount of n-dodecanethiol solution (40 mM) were injected into the solvent, the output frequency of the crystal decreased rapidly and then slowly to a flat with equilibrium in the bottom (called as F_1) like FD process (**Figure 1a**). It means that there are plenty of organothiol molecules adhered onto the gold substrate of QCM by Au–S bonding interaction. So this is the general organothiol self-assembled process ($F_1 < F_0$) under nitrogen with no disturbance of oxygen.
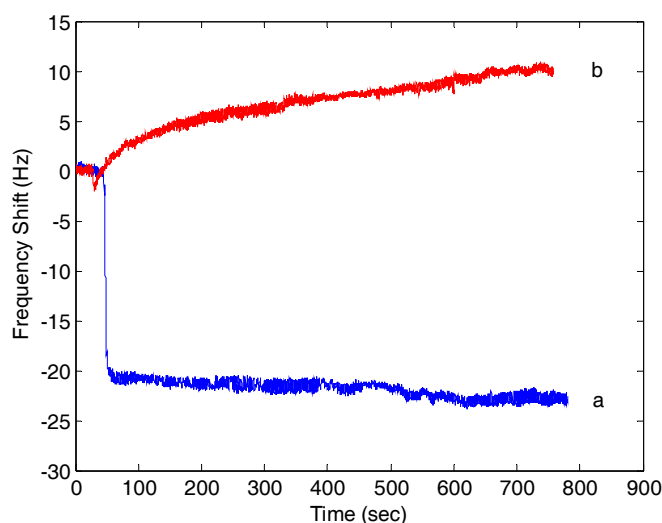

Figure 1   Typical kinetic response curves of n-dodecanethiol self-assembled on the surfaces of polycrystalline gold grains of QCMs in nitrogen (a) and oxygen (b) saturated THF solutions.

Existing of oxygen in THF solution, the frequencies turned to increase fast from the relatively stable equilibrium bottom (F_1) at first several minutes and then gradually reached to a relatively stable value (F_2) at a high stage in the oxygen ($F_2 > F_0$) saturated solutions, that was inverse to FD process. It suggested that something moved outside from the substrate of polycrystalline gold grains and dissolved in the solvent immediately after thiol adsorption, which was attributed to effect of gold corrosive dissolution induced by thiol and oxygen molecules. It was consistent with the work of Edinger et al [4, 5] that the gold corrosion was occurred in the presence of thiol compounds and oxygen, so the gold atoms could be brought out of the surface of polycrystalline gold grains by the corrosive oxidation.

There were many absolute proofs from AFM data for gold corrosion on the substrate of polycrystalline gold grains in the presence of thiol and oxygen. Prior to the formation of n-alkanethiol SAM, each gold grain of bared QCM could be indicated as the directions of a crystal facet due to its appearance of spheroid shape without any special planes. It possessed an average area of about 6400 nm^2 by examination of a grain size. The substrate changed on the atomic scale resolved images for n-dedocanethiol assembled polycrystalline gold grains in the nitrogen and oxygen saturated solutions are shown in **Figures 2a and 2b**, respectively. There were no obvious defects or holes only but many thiol growing grain substances in small size on the topmost surface layer of polycrystalline gold substrate in the nitrogen saturated solution (**Figure 2a**). On the contrary, there were many more noticeable defects or holes in the oxygen saturated solution (**Figure 2b**). It was undoubtedly attributed to the thiol-induced gold corrosion in the existing of oxygen which was in excellent agreement with the corresponding *in situ* QCM result, that the gold lost from the surface by corrosive oxidation and left many defects or holes on the gold grain surface, making the frequency increased to a high value (**Figure 1b**). From the section analysis of **Figure 2b**, it shows that the size of the corrosive holes are about 10 ~ 25 nm in diameter and 0.5 ~ 1.5 nm in depth.
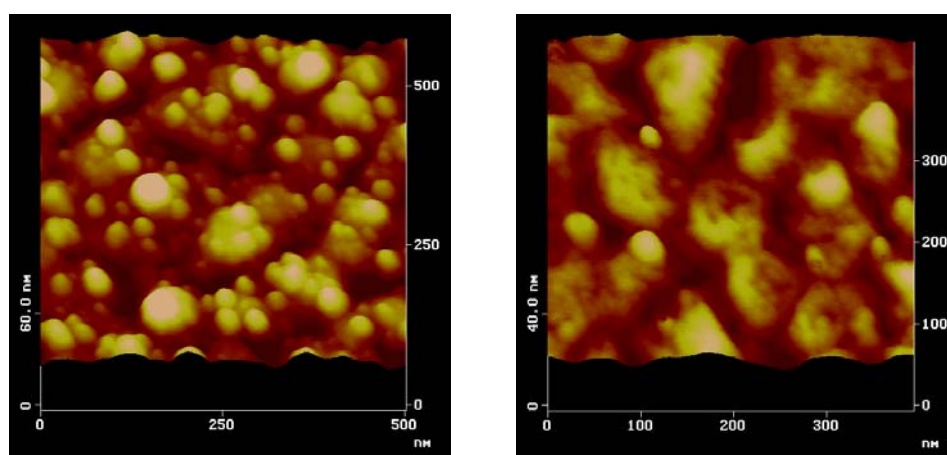

Figure 2 Typical SPM images for n-dodecanethiol SAM on the substrates of polycrystalline gold grains of QCM in the nitrogen (a) and oxygen (b) saturated THF solution.

As the increased frequency in the oxygen saturated solution was mainly caused by the corrosion of gold, a well linear increasing relation on the mass of gold loss with a modified logarithmic time scale can be obtained by the data fitting with the least square regression method that is listed below:

$$\Delta m = 7.9868 \cdot x - 11.8402 \qquad (1)$$

where $x = \log_{10}(t+44)$, Δm represents the mass of gold dissolved into the organothiol solution (ng), t is the time of gold corrosion (s). The linear regression coefficient is 0.9884 ($n=7290$). It was in nearly consistence with the result of atomic absorption spectroscopy determined by Edinger et al [4]. During the corrosion process, the maximum mass of gold atoms dissolved was estimated to be

approximate 11.6 ng indicating 8.7×10^{13} Au atoms/cm^2 left out of the QCM surface and disolved into the thiol solution from the QCM data. If only a monolayer of gold on the QCM surface (about 1.5×10^{15} Au atoms/cm^2) was oxidised, the mass loss of gold could be easily calculated to be approximately 5.8 % of a monolayer. Then the solubility of gold could be calculated to be 2.9×10^{-9} M, which the soluble product may be assumed to be Au−S−R. Besides that, a kinetic curve on corrosion rate of gold dissolved in the organothiol solution with the time of logarithmic scale is plotted in **Figure 3** by numeric differentiation of data. In brief, the initial corrosion was very fast and its rate was estimated to be about 9.2×10^{11} Au atoms cm^{-2} s^{-1}. The subsequent corrosion with a rate of about 5.4×10^{10} Au atoms cm^{-2} s^{-1} was at least one order of magnitude slower than the initial corrosion from the slope in **Figure 1b**. It shows that the required energy to break the crystal lattices of gold for its dissolution seems to be increase gradually, so the effect of gold corrosion tends to be gradually weak during the continuative oxidation process induced by the thiol molecules.
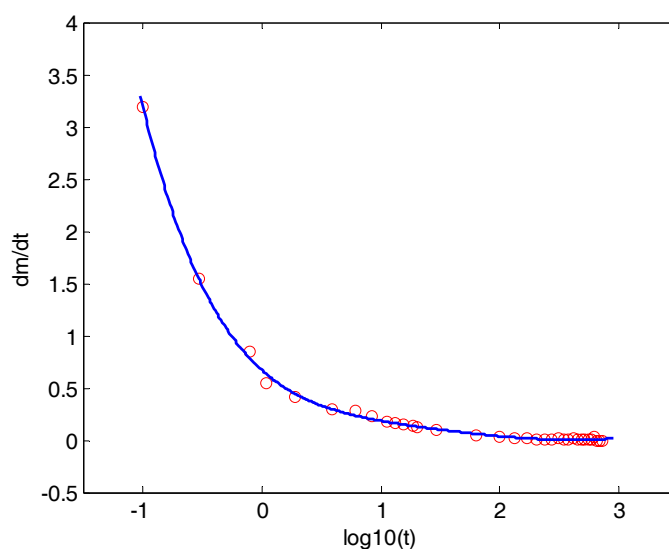

Figure 3 Kinetic curve on the gold corrosion rate.

References

[1] S. Krämer, R.R. Fuierer, and C.B. Gorman: Chem. Rev., Vol. 103 (2003), p. 4367

[2] R.L. McCarley, D.J. Dunaway, and R.J. Willicut: Langmuir, Vol. 9 (1993), p. 2775.

[3] G.E. Poirier and E.D. Pylant: Science, Vol. 272 (1996), p. 1145.

[4] K. Edinger, M. Grunze, and Ch. Wöll: Ber. Bunsenges. Phys. Chem., Vol. 101 (1997), p. 1811.

[5] K. Edinger, A. Gölzhäuzer, K. Demota, Ch. Wöll, and M. Grunze: Langmuir, Vol. 9 (1993), p. 4.