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In-situ analysis of stepwise self-assembled 1,6-Hexanedithiol multilayers by surface plasmon resonance measurements†

Soonwoo Chah,[a] Janos H. Fendler[b] and Jongheop Yi*[a]
[a] *School of Chemical Engineering, Seoul National University, San 56-1 Shinlim Kwanak, Seoul 151-742, Korea. E-mail: jyi@snu.ac.kr;swchah@hanmir.com; Fax: +82-2-885-6670; Tel: +82-2-880-7438*
[b] *Center for Advanced Materials Processing, Clarkson University, Potsdam, NY 13699, USA. E-mail: fendler@clarkson.edu; Fax: +1-315-268-4416; Tel: +1-315-268-7113*

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1,6-Hexandithiol (HDT) forms 6.9 ± 1.0 Å thick defect-free monolayers on gold substrates if the solution is purged by argon during the adsorption while long term (> 1000 min) exposure of the substrate to alcoholic HDT results in the stepwise formation of multilayers in the absence of argon purging.

Self-assemed monolayers (SAMs) of alkane dithiols are being increasingly employed as molecular wires and templates in the chemical construction of advanced electronic devices and sensors.[1,2] Defect free coverage of coinage metals (gold or silver) by a stable monolayer with an upright alignment of hydrocarbon chains is an important requirement for potential applications. The experimental conditions for self-assembly have drastic effects on the structure of the dithiol SAMs.[3–6] Depending on the preparation method, alkane dithiols have been shown to either adopt a fully extended flat configuration with the molecules lying parallel to the substrate, form upright monolayers at different tilt-angles, form covalently coupled multilayers, or undergo oxidation. Evidence is provided in this report for the self-assembly of 1,6-hexanedithiol, HDT, from a 1.0 mM alcoholic solution under both oxygenated and deoxygenated conditions. Fundamental data such as thickness, and the kinetics of layers formation, were also obtained by surface plasmon resonance (SPR) measurements.

HDT ($HS(CH_2)_6SH$, Aldrich), potassium ferrocyanide (Fisher), potassium chloride (J.T. Baker), ethanol (anhydrous, Pharmco), sulfuric acid (Fisher) and 30% hydrogen peroxide (Fisher) were used as purchased. The water used was purified using a Milli-Q™ Millipore system. Preparation of the Au SPR substrates is described elsewhere.[4–8] Briefly, Au films were deposited in a vacuum chamber (Edwards, AUTO 306) using Cr binder layers on clean microscope slides (Fisher Scientific, *finest Premium*, SF10, 3″ × 1″). The thickness of the Cr and Au films were monitored using a quartz crystal microbalance (QCM). Just prior to self-assembly, the substrates were cleaned by immersion into a Piranha solution and copiously rinsed by water and ethanol four times.

The time-resolved SPR measurements were carried out for the *in-situ* analysis of the HDT self-assembled layers using a 635 nm incident wavelength (using a 5 mW diode Power Technologies laser) and a bicell photodiode detector (Hamamatsu), following a previously described procedure.[9–11] In short, a cleaned gold substrate was attached to a SF10 prism (International Scientific Products) with index matching oil (R. P. Cargille Laboratories Inc.). A Teflon cell was adhered to the gold substrate to hold the self-assembly solution. A 5 mW diode laser was collimated and focused by a convex lens through the prism onto the gold substrate. The cell had an o-ring in the middle through which laser light contacted the self-assembly solution. Both the prism and the cell were mounted on a rotating plate to control the angles of the incident light. Prior to the measurements, the prism was rotated to determine the resonance angle where surface plasmon was at a maximum under ethanol in the cell. A bicell photodiode detector was used to detect the light reflected from the gold substrate at the resonance angle. The photocurrents from two photocells (A and B) were converted to voltages by a circuit. The reflected light detected at photocell A and B was then balanced by adjusting the photodetector position until $V_A - V_B$ approached zero. *In-situ* kinetic experiments were initiated by injecting 1 mM ethanolic HDT into the cell instead of ethanol. Data at the same point were collected every 30 s by a computer connected to the experimental apparatus using a homemade program. The ratio of the differential to the sum signals, which is linearly proportional to the SPR angular shift, was obtained numerically by dividing $V_A - V_B$ with $V_A + V_B$, and converted it into angular shifts (θ). The same experiments were carried out under both atmospheric and an inert (Ar) gaseous conditions to investigate the effect of oxygen on self-assembly. All experiments were performed at room temperature.

Fig. 1 shows the angular change (θ) of the resonance angle divided by the angular change at the surface-saturated point ($\theta_{saturated}$) after the self-assembly of 1 mM HDT on the gold substrate under both oxygenated and deoxygenated conditions. In both cases, SAMs were formed within 1 h on gold substrates (inset in Fig. 1). Subsequently, these conditions were maintained for 5000 min. After 1400, 2800 and 4600 min of self-assembly, abrupt increases were observed under atmospheric conditions, which shows that 1,6-hexanedithiol forms stepwise multilayers instead of a monolayer. On the other hand, only a monolayer was formed under the Ar gas condition. The same experiments were repeated four times (for phonomenological proof) after drying followed by the cleaning of the cell with water and ethanol. This supports the oxidative formation of a sulfur–sulfur bond by the insertion of oxygen from the air.[12]

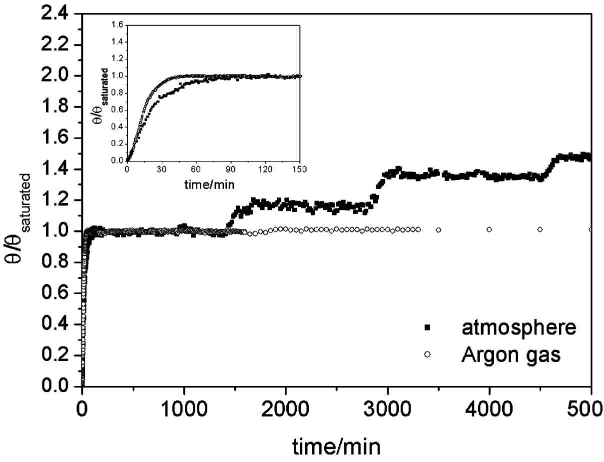

Fig. 1 SPR curve of 1,6-hexanedithiol (HDT) on a gold substrate as a function of time; HDT forms multilayers under atmospheric conditions (squares) while it forms monolayers under Ar gas (circles). The inset represents kinetics of initial self-assembly (monolayer-formation) under both conditions.

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† Electronic supplementary information (ESI) available: cyclic voltammogram of Au and HDT Au substrates. See http://www.rsc.org/suppdata/cc/b2/b206817f/

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The oxygen plays a role of a bridge between the dithiol molecules competing successfully with intralayer S–S bond formation. The fact that multilayers are not formed under inert gas condition supports indirectly the effect of oxygen on the formation of layers. The rate constants for each layer were calculated using a first order Langmuir adsorption model, as listed in Table 1. The formation rate (1.98×10^{-3} min^{-1}) of the HDT monolayer under Ar gas was similar to that (1.74×10^{-3} min^{-1}) under air. When the multilayers were formed, a remarkable change in the rate constants was observed. The rate constants of the multilayers were almost 30 times lower than that of the first layer. The differences in the bonding energies or stabilities of the S–Au or S–O–S bonds cause the differences between the rate constants of first layer and subsequent layers.

The thickness and the dielectric constant of the HDT SAM were estimated by angle-resolved SPR measurements, following a combined two-solvents method described previously.[13–15] Briefly, the uncoated side of the cleaned gold substrate was brought into optical contact with the base of a 90° glass prism, by means of index-matching oil (R. P. Cargille Laboratories, Inc.). A p-polarized light from a He–Ne laser (Hughes, 3222H-PC, 20 mW, 632.8 nm wavelength) was directed to the base of the prism, which was mounted on a stepping motor driven rotator (Oriel). It was capable of synchronously varying the angle of incidence, and the direction of a large area silicon detector (Newport, 818-SL) with an angle resolution of 0.01°. Each 20 s scan produced a reflectivity *vs.* incident angle curve under methanol and ethanol. The cleaned gold-coated substrates were immersed in the 1 mM 1,6-hexanedithiol solution for 90 min, followed by thorough washing with copious amounts of ethanol and water, and drying with gaseous nitrogen. The SPR plots were again recorded under methanol and ethanol. Using the known dielectric functions of a glass, a Cr film and a Au film,[16] and fitting the data to a standard five-phase model of reflectivity (based on the Fresnel equations), the unknown quantities were obtained. For the SPR spectrum of the gold substrate saturated with HDT in methanol, the calculated dielectric constant ranged from 1.921 to 3.792 (solid line with squares in Fig. 2) depending on the film thickness. However, the SPR spectrum for the same substrate measured in ethanol produced a different set of thickness–dielectric constant pairs (solid line with triangles in Fig. 2) except for one point, where the lines intersected. If the structure and thickness of the substrate are assumed to be same in both solvents, the point of intersection provides the true average dielectric constant and the average thickness of the substrate, which are 2.25 and 6.9 ± 1 Å for the monolayer, respectively. With the same methodology, the average dielectric constant and the average thickness of the bilayer could be estimated to be 2.38 and 8.3 ± 1 Å. Thicknesses of monolayer and bilayer correspond to the height difference shown in Fig. 1. According to Chempen3D software (Hilton), the molecular length of the HDT was estimated to be 10.9 Å. Therefore, from Fig. 1 and Fig. 2, the HDT-monolayer was estimated to be tilted by 39°. The second layer was either more tilted (7.4° to the plane) or parallel to the first layer. In addition, the electrochemical behavior of the HDT monolayer as a function of the electrode potentials (−0.1 to 0.5 V) was examined in a mixed solution of 1 mM potassium ferrocyanide and 0.1 M potassium chloride. When compared with bare Au, the HDT covered gold substrate exhibited a markedly lower charging current, which is characteristic for thin layers with a low dielectric constant blocking ion transfer to the electrode (see ESI†). From this result, it was inferred that 1,6-hexandedithiol formed a defect-free monolayer on Au. Although the formation of disulfide multilayers has already been reported in the paper by Blanchard' group,[12] *in-situ* analysis has to date not been reported by surface plasmon resonance measurements, and reveals that HDT multilayers are formed stepwise under atmospheric conditions.

Table 1 Kinetics of layers formed under Ar or under air

Condition	Layers	Rate constant, k/min^{-1}
Monolayer formation under Ar	Monolayer	1.98×10^{-3}
Multilayer formation under air	1st layer	1.74×10^{-3}
	2nd layer	6.80×10^{-5}
	3rd layer	5.60×10^{-5}
	4th layer	5.30×10^{-5}

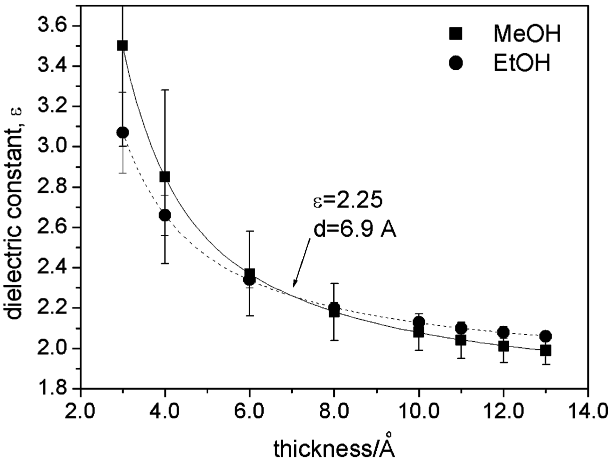

Fig. 2 Film dielectric constants and thicknesses for a 1,6-hexanedithiol monolayer. The film thickness (6.9 Å) and dielectric constant (2.25) are determined from SPR measurements in methanol (squares) and ethanol (circles).

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