Critical thermal variation of displacement of alkanethiols in self-assembled films

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Abstract

A packed structure of hexadecanethiol (HDT) self-assembled monolayer (SAM) on the polycrystalline gold electrode was reportedly loosed at temperature more than $T_C = 45$ °C. In this paper, the looseness was examined through the displacement of some longer alkanethiols by propanethiol (PT) in ethanol solution. As a measure of the looseness, capacitance, C, by the ac impedance was obtained under cyclic scanning variations of temperature, T, between 0 and 70 °C. Curves of C vs. T at the HDT SAM showed no hysteresis in ethanol solution as well as HDT solution. However, C vs. T curves of the HDT SAM in the PT ethanol solution increased drastically at temperature ($T_D = 53$ °C) higher than T_C to approach gradually the capacitance value of the PT SAM, indicating the displacement of the HDT by PT. Values of T_D were independent of the chain length, whereas those of T_C decreased with a decrease in the chain length of alkanethiols. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Self-assembled monolayer (SAM) films of alkanethiols coated on a gold surface are stabilized not only by the strong adsorption of the thiol group on gold atoms [1,2] but also by the strong interaction among alkane chains [3,4]. The latter interaction is reminiscent of the interaction of crystallization energy of polyethylene [5,6], and hence awakes our interest in crystalline structure and its phase formation. It is not easy, however, to detect and identify the formation of a macroscopic domain [7,8]. A binary composite SAM is a nice system of investigating domain formation because a domain is regarded as a reference domain in order to discriminate it from the other. In fact, some binary SAMs have shown phase-separated domains [9–13], and some have exhibited only a homogeneous domain [14–18].

A variable of causing phase separation is temperature. A few studies have directed to temperature-dependence of SAMs, e.g., thermal effects on interactions [7], phase transition [8,19] and phase formation [20,21]. A reason of few number of reports is small and poor reproducible dependence of optical and electrochemical signals on temperature especially for long time measurements. Some work on the temperature-dependence has aimed at evaluating activation energies of the desorption from metal surfaces [22–25], chemical reactions at SAMs [26–28], and heterogeneous reactions through SAMs [29,30].

Previously, we obtained long-term variations of differential capacitance of the hexadecanethiol (HDT) film adsorbed on a polycrystalline gold surface, and found that the capacitance data were sensitive to temperature [31]. The sensitiveness varied critically at a given temperature, denoted by T_C, exhibiting the behavior like phase transition [19]. The increase in the capacitance at $T > T_C$ indicates looseness of the packing of the SAM. It is predicted that the loose packing displaces the HDT chains by other alkanethiols in the solution even if other alkanethiols are shorter than HDT. Properties of the displacement at room temperature have been well documented [14], and have been applied to investigation on formation of domains [9,11,32]. This paper reports variations of the capacitance of alkanethiol SAMs with temperature in some solutions in order to find the possibility of the displacement.

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2. Experimental

All chemicals were of analytical grade and commercially available. A polycrystalline gold disk electrode, 1.6 mm in diameter, was used as a substrate of the SAM. The reference and the counter electrodes were, respectively, a Ag/AgCl electrode and a platinum coil.

A home-made potentiostat was employed, which was controlled with a computer via 12-bit D/A and A/D converters (aISA-A57, Adtek) with the help of a home-made software. For measurements of capacitance, an ac voltage, E_{ac}, from a lock-in amplifier (Model-5210, EG & G) was superimposed on the dc voltage, $E_{dc} = 0.3$ V, which was close to a point of zero charge of the HDT SAM [31]. The output current was analyzed with the lock-in amplifier to yield real, I_R, and imaginary, I_M, components. The capacitance, C, was evaluated from the slope of the plot of $I_M[(I_R/I_M)^2 + 1]$ against ac frequency, f, through the expression:

$$I_M[(I_R/I_M)^2 + 1] = 2\pi E_{ac} C f \tag{1}$$

on the assumption of a series combination of a capacitance and a resistance [33,34]. The value of E_{ac} was 10 mV. After the linearity of the plot was confirmed at a given electrochemical system, values of C at the temperature-scan experiment were obtained at 500 Hz in order to acquire a number of data points at a short time.

Capacitance was measured in 0.10 M tetramethylammonium chloride (TMACl) ethanol solution, 0.10 M TMACl + 10 mM HDT ethanol solution, 0.10 M TMACl + 10 mM propanethiol (PT) ethanol solution, or 0.15 M KCl aqueous solution, unless otherwise mentioned. The solution was stirred with a magnetic stirrer at 60 rpm. The temperature was controlled with an adequate combination of an electric heater and ice so that temperature-scan rates were 0.17 and -0.09 °C s^{-1} at the ascending and the descending variation, respectively.

After the electrode was polished with a suspension of alumina powder (2000 meshes), sonicated in an ion-exchanged water, and rinsed with acetone, it was immersed into 10 mM alkanethiol ethanol solution for 12 h to generate a thiol SAM. It was immersed into ethanol for 10 min to remove the alkanethiol which was adsorbed physically on the SAM. It was transferred to the thermostatic electrochemical cell, and the capacitance was measured until its value reached a steady-state, typically for 6 h. This process gave reproducible data.

3. Results and discussion

Variations of $I_M[(I_R/I_M)^2 + 1]/2\pi E_{ac}$ for the HDT and the PT SAMs with f showed an approximately proportional line including slightly concave shape in the domain $600 < f < 1000$ Hz, as shown in Fig. 1. The concave shape is ascribed to the non-accurate approximation of
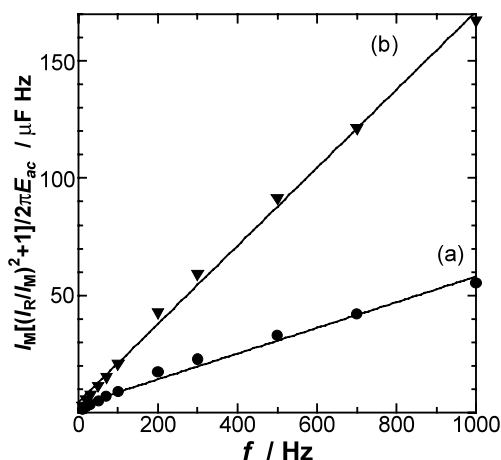

Fig. 1. Variations of experimental values of $I_M[(I_R/I_M)^2 + 1]/2\pi E_{ac}$ for (a) the HDT and (b) the PT SAMs with f.

the series combination of a resistance and a capacitance owing to heterogeneity of the SAMs [31]. SAMs with short alkane chains are said to be unstable [3]. So far as we varied frequency at a given PT SAM, the capacitance values were stable. Therefore the frequency-dependence shows behavior close to the ideal capacitance.

Capacitance values, C, of HDT and PT in the 0.15 M KCl aqueous solution increased with an increase in temperature, T, as shown in Fig. 2. This kind of the increase can be found also at a bare gold electrode [19]. There was little hysteresis in the curves at the forward (ascending) and backward (descending) temperature scans for HDT and PT SAMs (Fig. 2), suggesting an almost steady state in the time scale of ca. 20 min for a temperature cycle. The capacitance of PT, C_3, was ca. four times larger than that of HDT, C_{16}. If the capacitance is assumed to be inversely proportional to the number of carbons and sulfur, the ratio of the capacitances is given by
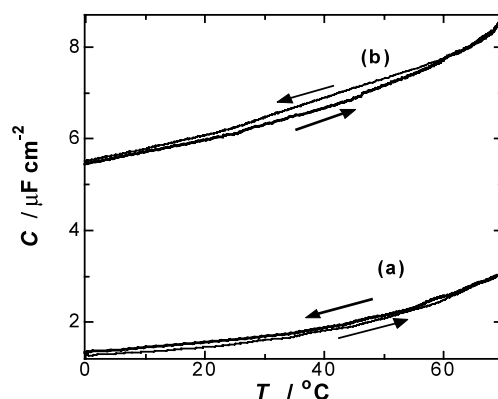
$$C_3/C_{16} = 17/4 = 4.3. \tag{2}$$

Fig. 2. Temperature-dependence of capacitances of (a) HDT and (b) PT SAMs in 0.15 M KCl aqueous solution. Arrows are directions of temperature scans.
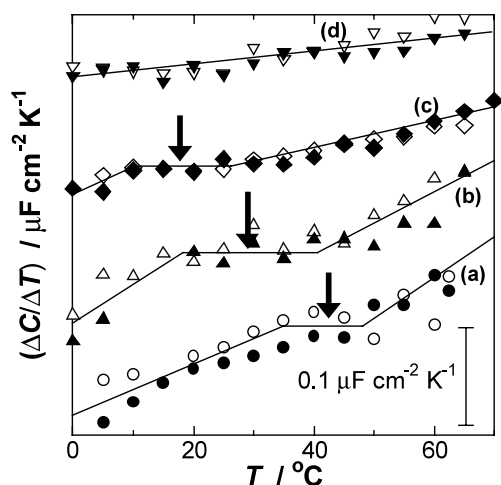
Fig. 3. Dependence of $\Delta C/\Delta T$ on T for (a) HDT, (b) tetradecanethiol, (c) dodecanethiol and (d) PT SAMs at the forward (open marks) and backward (full marks) temperature scans in 0.15 M KCl aqueous solution. Arrows point an average temperature of two inflections of the lines, representing T_C.
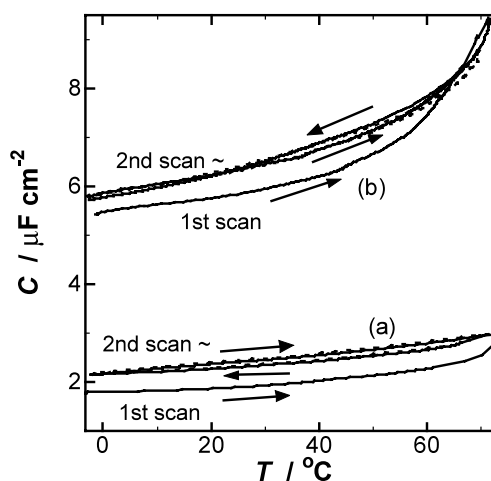

Fig. 4. Temperature-variations of the capacitance of (a) the HDT and (b) the PT SAMs in ethanol solution including 0.1 M TMACl. Dashed curves are for the second backward and the third forward scan.

This is close to the experimental value of the ratio, as has been demonstrated for various lengths of alkanethiols [3].

Curves in Fig. 2 look monotonic and featureless. Taking differentiation, dC/dT, has exhibited a specific feature [19]. In order to reduce noises in numerical differentiation, we replaced the differentiation by finite difference among five points [19]. Variations of $\Delta C/\Delta T$ thus obtained were plotted against T in Fig. 3 for HDT, tetradecanethiol, dodecanethiol and PT SAMs. We see from Figs. 3(a)–(c) that variations of $\Delta C/\Delta T$ with T except for PT were composed of three parts. For example, values of $\Delta C/\Delta T$ for HDT at $T < 40$ °C and $T > 50$ °C fall on each straight line, which varies largely in the domain $40 < T < 50$ °C. Large scatter occurred at $T > 60$ °C because of generation of gas bubbles near the electrode. We stand for this temperature domain as the average value, 45 °C, and denote it as T_C. Values of T_C decreased with a decrease in the number of carbons of alkanethiols (n), as shown in Table 1. Those for $n < 12$ could not be obtained because they are out of the measurement range. Since values of $\Delta C/\Delta T$ vary drastically near T_C, we can regard T_C as a temperature relevant to a transition of the looseness. The increase in T_C with an increase in n indicates that T_C should be related

Table 1
Values of T_C and T_D for alkanethiols

n	T_C (°C)	T_D (°C)
10	–	48
12	17	55
14	26	58
16	45	53

with interaction energy between methylene groups of closest neighboring chains, like melting temperatures.

The temperature variation of the capacitance was measured also in ethanol solution including 0.1 M TMACl, and was shown in Figs. 4(a) and (b) for HDT and PT, respectively. The C vs. T curve at the first forward scan was lower than those at the first backward and further scans, although the SAM was immersed into the ethanol solution at room temperature for 6 h before the measurement of the capacitance. Little hysteresis was found at the second and the succeeding scans. The enhancement of C at the second and the succeeding scans may be ascribed to desorption of extra-adsorbed species by the increase in temperature over the T_C at the first scan. In other words, an extra-amount of alkanethiols is adsorbed on the Au in 10 mM alkanethiol ethanol solution when the SAM is prepared at room temperature. The extra-amount is dissolved in ethanol solution by thermal activation (Fig. 4) but is not dissolved in the aqueous solution (Fig. 2).

The compact structure of the SAM loosens for $T > T_C$, and hence the adsorbed chains may be desorbed or displaced by other adsorbates present in solution. In order to examine a possibility of the displacement, we scanned temperature in the HDT SAM in the solution including HDT or PT. The C vs. T curve in the ethanol solution including 10 mM HDT (Fig. 5(a)) shows a variation smaller than the curve without HDT (Fig. 4(a)). This is because the desorption especially for $T > T_C$ is compensated with the re-adsorption of HDT from the solution. In contrast, the capacitance of the HDT SAM in the ethanol solution including 10 mM PT began to increase at the temperature slightly larger than T_C (Fig. 5(b)) for the forward temperature scan, and was enhanced drastically at $T > 60$ °C. This increase can be explained by the displacement of the HDT SAM by PT
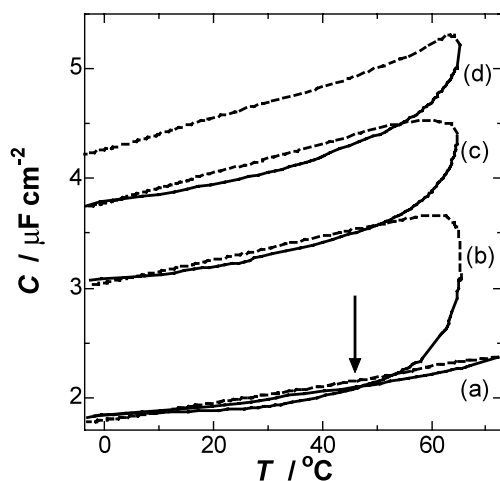
Fig. 5. Temperature-variations of the capacitance of the HDT SAM in the 0.1 M TMACl ethanol solution including: (a) 10 mM HDT, (b) 10 mM PT at the first, (c) 10 mM PT at the second and (d) 10 mM PT at the third scan. The arrow represents T_C for the HDT SAM. Solid and dashed curves are for the forward and the backward scan, respectively.

in the solution. We denote the onset temperature for the displacement as T_D. Since the desorbed HDT diffuses to the bulk solution so that the surface concentration is almost zero, the re-adsorption may not occur actually at $T < T_D$. Therefore, the capacitance at the backward scan decreases, showing a slower slope. The forward iterative scans also increased the capacitance largely for $T > T_D$, whereas the capacitance at the backward scan showed still the slow slope. The enhancement for $T > T_D$ at the forward scan decreased with the number of the scans, implying that the enhancement should be associated with a long-term relaxation for the displacement at $T > T_D$.

In order to examine the slow relaxation, time-variations of the capacitance were observed for four combinations of: (a) the HDT SAM in HDT solution, (b) the PT SAM in PT solution, (c) the PT SAM in HDT solution, and (d) the HDT SAM in PT solution at room temperature. As shown in Fig. 6, capacitances in cases (a) and (b) showed virtually no time-variations. The adsorption equilibrium has been completed at $t > 1000$ s. When the PT SAM was transferred into the HDT solution (c), the capacitance decreased rapidly and tended to the capacitance for the HDT SAM in the HDT solution (a). This fact suggests the displacement of the PT SAM by HDT. In contrast, the capacitance at the HDT SAM in PT solution (d) slightly increased at very slow rate, and has not reached a steady-state capacitance even at 6 h at room temperature.

The time-variation of the capacitance for the last combination was obtained at several temperatures, and was shown in Fig. 7. Values of C increased not only with the time but also temperature. The increment, $C(t) - C(t = 0)$, can be approximated as a contribution of the capacitance of only the PT SAM because of
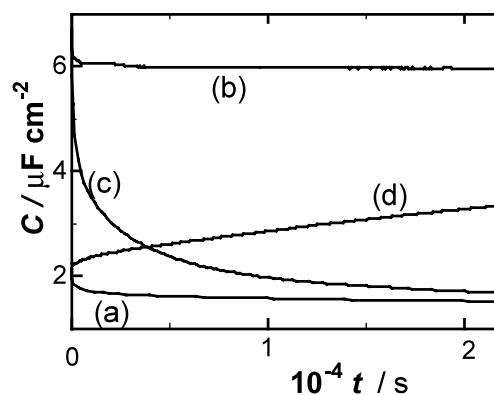

Fig. 6. Time-variations of the capacitance of: (a) the HDT SAM in HDT solution, (b) the PT SAM in PT solution, (c) the PT SAM in HDT solution, and (d) the HDT SAM in PT solution at room temperature. The ethanol solution also included 0.1 M TMACl.
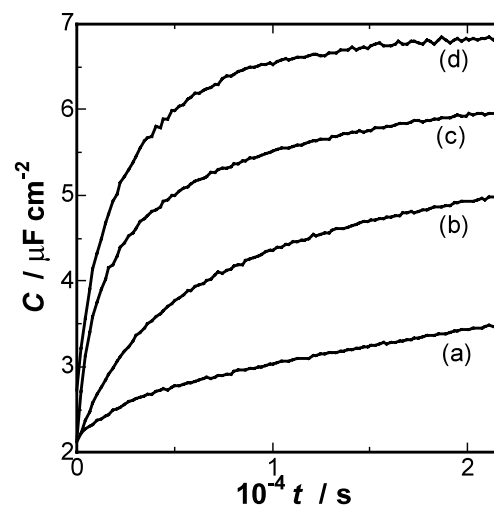

Fig. 7. Time-variations of the capacitances of HDT SAMs at (a) 15 °C, (b) 30 °C, (c) 40 °C, and (d) 45 °C in the ethanol solution including 10 mM PT and 0.1 M TMACl.

$C_3 \gg C_{16}$. By use of the experimental result of $C_3/C_{16} = 4$ (similar to Eq. (2)), a capacitance value of a completely displaced SAM by PT would be 7 μF cm^{-2}. An increase in temperature more than 45 °C may give rise to the partial displacement at such a short time as the temperature-scan period of Fig. 5. It took more than 5 h to displace most of HDT by PT at 45 °C. However, the displace experiment at $T > 45$ °C includes errors for long time measurements because PT is evaporated to reduce the concentration.

We evaluated T_D for other alkanethiols displaced by PT, and show them in Table 1. Values of T_D were almost independent of n, and hence are essentially different from T_C. The independence of n indicates that the displacement is not ascribed to the chain–chain interactions characterizing T_C, but is to the interaction between the sulfur and gold. Since conventionally employed alkanethiols are $n \leqslant 18$, we can deduce that $T_C < T_D \approx 54$ °C.
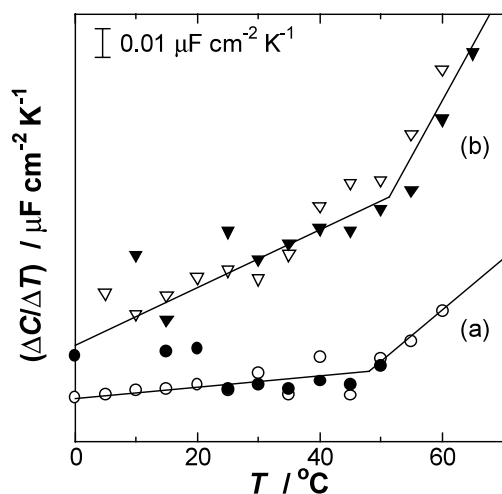
Fig. 8. Variations of $\Delta C/\Delta T$ with T obtained from Fig. 4 for (a) the HDT and (b) the PT SAM in the 0.1 M TMACl ethanol solution. Open marks are at the forward scan whereas full marks are at the backward scan.
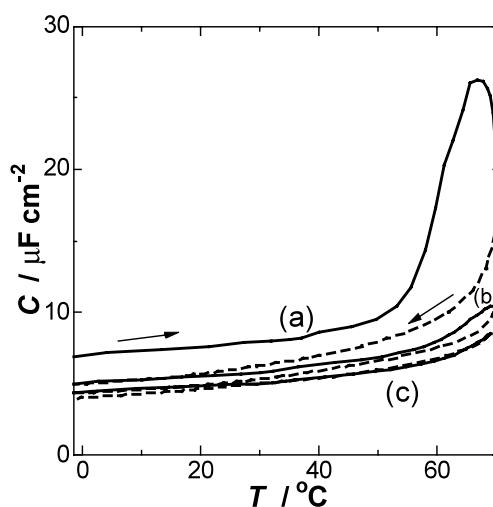

Fig. 9. Temperature-dependence of the as-prepared PT SAM in 0.1 M TMACl ethanol solution at the (a) first, (b) second and (c) third scan. The solid and dashed curves are at the forward and the backward scan, respectively.

This relation implies that any SAM is soon displaced by other alkanethiols present in solution when $T > T_D$. The displacement of any alkanethiol at $T > T_D$ seems to be inconsistent with the fact that longer alkanethiols are adsorbed more strongly [7]. However, the dependence of the amount of the adsorbate on the chain length is emerged only for $T < T_C$.

It is expected that T_D is also found from the SAMs in the ethanol solution by taking $\Delta C/\Delta T$ in Fig. 4. The plots of $\Delta C/\Delta T$ against T for the HDT and the PT SAMs are shown in Fig. 8. Slopes of the lines change at 50 °C for both SAMs. This temperature is close to values in Table 1.

The displacement necessarily includes desorption of alkanethiols from a SAM and adsorption of other alkanethiols from solution. Similar behavior may be predicted in the rearrangement of alkanethiols on a SAM, the process including the desorption, transfer from a adsorption site to the other, and the adsorption. In order to make the rearrangement feasible and detectable, we examined temperature-variation of the as-formed PT SAM into the stabilized SAM which would be the same as the SAM 6 h left at room temperature. Fig. 9 shows variations of C_3 with temperature at the first three scans. The capacitance increased drastically at ca. 55 °C with an increase in temperature. However, it decreased at $T > 65$ °C even at the forward scan. The capacitance values at the second and the third scan, especially for $T > 50$ °C were much smaller than that at the first scan. These temperature-variations can be considered to be the rearrangement of propanethiol chains to more stable sites by iterative processes of desorption and re-adsorption. The temperature at which the rearrangement occurs is close to T_D. The similarity of T_D values for the displacement and the rearrangement indicates

that the rearrangement is also controlled by the interaction energy between gold and sulfur.

Of interest is discussion of T_D in a line of some reported factors which are mainly responsible for displacement. It is reported that a critical factor of displacement is compactness of SAMs on the basis of the relation between displacement rates and size of thiols [35]. Since the compactness is relevant to the chain–chain interaction rather than the S–Au interaction, it may be out of the significance of T_D. However, the compactness obviously plays an important role in kinetics of displacement. Displacement is readily commenced at defect sites [36] or phase boundaries [37]. Since defect sites, especially at a peripheral of a domain, are generally active, they may break S–Au bonds to lead displacement. This is consistent with the significance in T_D. The S–Au interaction is crucial for pattern formations [38]. This agrees with our conclusion.

4. Conclusion

An alkanethiol SAM has a specific temperature, T_C, over which $\Delta C/\Delta T$ varies largely with inflection points owing to the transformation into a loose structure. Values of T_C increase with the chain length of alkanethiols by 6 °C per methylene group. Although the loose structure seems to promote displacement of the SAM by other alkanethiols, the displacement occurred at a temperature (T_D) independent of the chain length. A SAM of a longer chain is displaced rapidly by a SAM of a shorter chain at $T > T_D$. In other words, any SAM can be displaced by alkanethiols present in solution at $T > T_D$ at a short time. This displacement is a convenient technique of modifying SAMs. The displacement

looks thermodynamically unreasonable. However, it is ascribed to the infinite dilution of the displaced (long) alkanethiol to the solution.

As has been described in Section 1, SAMs are stabilized with both the chain–chain interaction and the sulfur–gold interaction. These interactions have been specified quantitatively by T_C and T_D in this study. The fact $T_C < T_D$ is consistent with the following conventional image: when temperature increases, the chain–chain interaction is loosened, the sulfur–gold bond is broken, and then alkanethiols are desorbed from the electrode.

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