A Method To Study the Phase Transition and Desorption of Self-Assembled Monolayers on Planar Gold Surfaces

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In-plane resistance of thin gold films (thickness ∼1000 Å) after the formation of self-assembled monolayers has been measured as a function of temperature. We attribute the observed increase in the slope of the resistance vs temperature plot in the case of octadecanethiol and octanethiol monolayers at characteristic temperatures to phase transitions. The structural transition of 1,4-benzenedimethanethiol is also manifested similarly. Propanethiol does not show any phase transition, as expected. The observed changes in the alkanethiol monolayers are related to the decrease in the lifetime of the parallel vibrational motion of the adsorbate on the gold surface. The increase in slope is followed by a decrease which is attributed to the commencement of desorption of monolayers from the gold surface.

Self-assembled monolayers (SAMs)[1] on noble metal surfaces have become model systems for studying organic interfaces. These well-organized molecular assemblies find use in a wide range of applications.[2] The structure of these monolayers has been characterized by various spectroscopic techniques.[3] Studies of interfacial phenomena including wetting,[4] electron transfer,[5] adhesion,[6] molecular recognition,[7] etc., have been performed with these

surfaces. However, there is a need to study them by simple techniques principally from the point of view of routine structural characterization. Upon increase in temperature, these crystalline assemblies undergo phase transitions.[8] Order/disorder transitions in them have been reported at low and high temperatures.[9] Thermal motions of the terminal methyl groups in long-chain thiol monolayers have been observed in low-energy helium diffraction.[10] Batia and Garrison[11] performed theoretical calculations on the phase transitions of C_{13} thiol monolayer on gold. They observed two phase transitions, one below room temperature (around 275 K) attributed to the change in tilt direction from nearest neighbor to next nearest neighbor and another gradual one attributed to the irreversible melting transition starting at 350 K and extending up to 400 K. Bensebaa et al.[12] did detailed temperature-dependent studies on SAMs to probe the different phases using reflection absorption infrared spectroscopy (RAIRS). They observed an orientational transition for C_n ($n = 15−22$) monolayers, starting around 350 K and extending up to 400 K. They also found that the solid-to-liquid melting transition observed in SAMs is irreversible. Exact transition temperatures are not known experimentally.

Resistivity as a tool to understand SAM formation was first reported by Rubini.[13] He used thin-film conductance to characterize the chemisorption of thiols and disulfides on metal surfaces.

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Recently Zhang et al.[14] showed that mercaptan chemisorption at a liquid−gold film interface can be probed by in-plane resistivity measurements. When the film thickness (*d*) was between the onset of conductivity (∼5 nm) and the electron mean free path (∼80 nm), they observed an increase in the in-plane resistivity as a monolayer was formed on the gold surface that was correlated to the effect of surface dipoles on the diffuse scattering of charge carriers at the solid−liquid interface.[14]

Persson and co-workers[15] extensively studied the change in surface resistivity of thin metal films upon adsorption of molecules on the film surface. The increase in surface resistivity is related to the diffuse scattering of conduction electrons in the metal from adsorbates. They derived a relation between the increase in the resistivity $\Delta\rho$ of a thin metal film upon adsorption of molecules on its surface and the lifetime τ of the parallel vibrational motion of the adsorbate—the so-called parallel frustrated translation due to the excitation of electron−hole (e−h) pairs. The fundamental relation is,

$$1/\tau = (n^2 e^2 / M)\, d\, \partial\rho/\partial n_a|_{n_a = 0} \;\;(1) \qquad (?)$$

where M and n_a are the adsorbate mass and number density, respectively, d is the film thickness, n and e are the electron number density and charge, respectively, and $1/\tau$ is the adsorbate vibrational damping rate due to the excitation of electron−hole pairs. $\partial\rho/\partial n_a|_{n_a = 0}$ is the initial (as $n_a = 0$) slope of the increase in film resistivity ρ with increasing adsorbate concentration, n_a. The damping of vibrations of adsorbed molecules is a simple dynamic process at a surface, and the damping rate is an important parameter for studying surface-activated processes such as desorption or diffusion.[15a]

In this paper, we report simple four-probe resistance measurements used for the study of phase transition and desorption of self-assembled monolayers on gold surfaces. We measured change in resistance as a function of temperature of the monolayer-covered gold surfaces. There have been studies on the resistivity of thin pure gold films up to 300 K[16] which show that the resistivity increases linearly with temperature. The observed increase in resistivity is attributed to the increased electron−phonon interactions. We observed a linear increase in resistance for pure gold film up to 450 K. For the alkanethiol-modified gold surfaces, we observed a small deviation in the relative resistance from the linear behavior, above 330 K for an octanethiol (OT) monolayer and above 360 K for an octadecanethiol (ODT) monolayer. We attribute this increase in the slope of the resistance vs temperature plot to the phase transition occurring in the monolayer. This small increase in slope is followed by a decrease due to gradual desorption of the monolayer. We also performed similar measurements for propanethiol (PT) and 1,4-benzenedimethanethiol (BDMT) monolayers on gold surfaces. We have observed a clear increase in the slope attributed to the structural transition in the case of BDMT monolayers. For the PT-modified gold surface, only a decrease in slope at high temperature due to desorption of the monolayer was observed.

EXPERIMENTAL SECTION

Propane-, octane-, octadecane-, and 1,4-benzenedimethane thiols were purchased from Aldrich Chemical Co. and were used as received. All monolayers were made with 1 mM thiol solutions in methanol. The gold plates for the measurements were prepared by sputter coating gold on 2 × 2 cm glass slides. First, the glass slides were cleaned with chromic acid solutions and were washed thoroughly with copious amounts of ultrapure water. These plates were then sonicated for 1 h in water. The plates were dried and introduced into an Edwards sputter coater. A base layer of titanium was coated first for better adhesion followed by gold. The coating was done in argon atmosphere at pressures below 1×10^{-1} mbar. The current and voltage were kept at 4 mA and 1.5 kV, respectively. Titanium was coated for 10 min followed by gold for 30 min. The gold and titanium used for coating were 99.8% pure. Grain boundaries and point defects in the films were removed by annealing them at 600 K for ∼10 h.[17] From destructive chemical analysis, the thickness of the gold film was estimated to be ∼1000 Å. An accurately weighed gold-coated glass plate was taken and the gold film (along with the Ti base layer) was dissolved in aqua regia. The glass plate was weighed again accurately. Assuming uniform coverage, the thickness of the gold film was calculated from the difference in weight, area of the film, and density of bulk gold.

The flow cell for resistance measurements was constructed as follows. A Teflon rod of 2-cm height and 2.5-cm diameter was taken. A hole of 8-mm diameter and 10-mm depth was made in it. Two holes of 1-mm diameter on either side of the rod were made for the passage of the thiol solution. Four more holes of 1-mm diameter were made on the wall of the Teflon cell to insert the four gold wires. In-plane resistance measurements were done by keeping the gold plate above the cell with a viton O-ring as the liquid seal. The gold plate was pressed such that it was in contact with the four gold wires. A schematic of the cell is shown in Figure 1. Variable-temperature measurements were conducted by placing a heating block right above the glass plate. The temperature was measured close to the glass plate. The temperature was increased gradually at a rate of ∼1 °C/min. Data were measured while heating.

Monolayers were prepared by exposing a 1-mm solution of the corresponding thiols in ethanol to the gold films fixed on the flow cell. The solution was continuously run for 12 h through silicone tubes connected to a peristaltic pump. The flow rate was maintained at 100 cm³/h. Simultaneously, the resistance was measured by connecting four gold wires to the four probes of a Keithley model 2001 multimeter. The injected current was 9.3 mA. The resistance ($R = V/I$) was read out directly from the multimeter, which was interfaced with a computer. The temperature-dependent measurements were done without disturbing the setup, but in a constant flow of high-purity argon. The films

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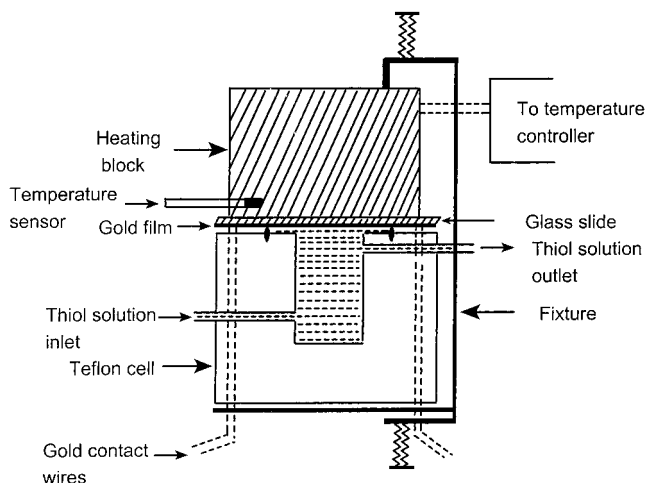
Figure 1. Schematic diagram of the experimental setup for the four-probe resistance measurement.

Figure 2. Initial increase in the slope of the resistance vs time plot when thiol solutions are exposed to Au films: (a) ODT; (b) BDMT. The noise level during the measurement was less than 0.0001 Ω. The resistance plotted is relative ($R/R_o - 1$), where R and R_o refer to the resistance of the thiol exposed and the pure gold films, respectively.

(formed in the cell, 12 h of continuous exposure) were repeatedly washed with ethanol and dried with argon in situ in the flow cell. The viton O-ring was covered with a Teflon tape to protect it from damage at high temperatures and also to protect the thiol solutions from contamination. Resistances were measured when equilibrium in the temperature setting was achieved.

Earlier studies[9b,12,18] from this and other laboratories have shown that alkanethiol monolayers begin to desorb above 350 K. BDMT monolayers desorb above 473 K, although slow desorption commences even below this temperature. Below the desorption temperature, the monolayer concentration is not significantly affected by temperature cycling. In agreement with this, the resistance values recovered below 350 K. However, after the phase transition, the features observed in the resistance curves were not reproducible, consistent with the RAIRS study.[12]

RESULTS AND DISCUSSION

As observed by Zhang et al.,[14] we observed a small increase in resistance when gold films were exposed to ethanol solutions and a decrease when the films were exposed to argon. Increase in the slope of the resistance vs time plot was more when the gold surface was exposed to thiol solutions. The slope increased rapidly initially and thereafter it remained constant. Figure 2 displays the plot of relative resistance vs time for ODT- and BDMT-exposed gold films. Delay in the onset of increase is due to the time taken for the thiol solution to reach the cell. The initial increase in resistance is due to chemisorption of thiols on the gold surface. The increase in resistance is abrupt when the gold film was exposed to alkanethiols, whereas the resistance increases only to three-quarters of the alkanethiol value when exposed to aromatic thiols. This difference between aliphatic and aromatic thiols is in accordance with the earlier observation by Zhang et al.,[14] where hexadecanethiol was compared with benzenethiol. This clearly shows the reproducibility of the method. The difference in observed resistance between the long-chain thiols
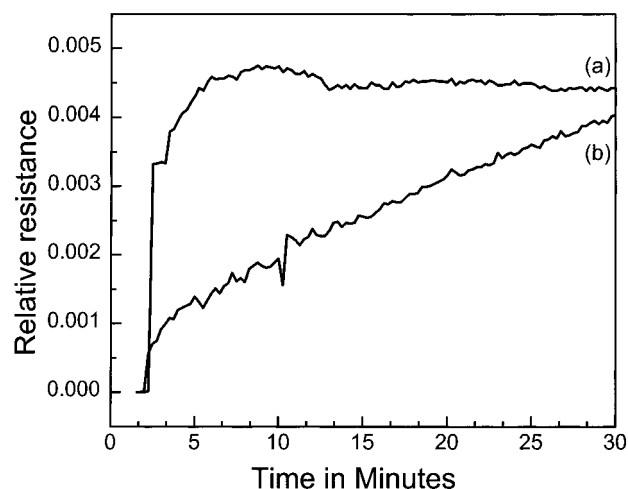
and the aromatic thiols is explained on the basis of the extent of electronic interaction.[10] A Newns−Anderson model for chemisorbed species is used to explain the observed differences.[14] OT and PT show behavior similar to that of ODT (not shown). Whereas the increase in resistance for the alkanethiols is abrupt, occurring over the first 2 min of exposure, increase in the case of BDMT is slow and saturates at ~50 min of exposure. It appears that all the possible surface sites are occupied by the alkanethiol molecules spontaneously. In the case of BDMT, the adsorption initially occurs in a bent geometry,[19] giving a reduced monolayer density. The structural change to a more perpendicular orientation and subsequent increased coverage occurs slowly, resulting in a slow increase in the slope. Thus, it is obvious that *surface resistivity is a probe to understand the kinetics of chemisorption/self-assembly at least in certain systems.*

The experimental data have been reproduced several times; the extent of increase in resistance varied between different samples due to variation in metal film thickness, which was difficult to be kept constant in sputter evaporation. The extent of increase observed upon alkanethiol adsorption is smaller compared to the report of Zhang et al.,[14] and this is attributed to the greater thickness of the Au films used in this study. Prolonged annealing of the gold films helped in the reproducibility of the measurements.

Figure 3 shows the resistance vs temperature plots for the pure gold film and the ODT monolayer-covered gold surface. The resistance values are relative to the room temperature value. It is clear from the plot that the slope of the resistance vs temperature curves of the pure gold plate varies almost linearly with temperature. The resistance for the ODT monolayer varies linearly up to 360 K, and then it increases more rapidly up to 380 K. After 380 K, we observed a decrease in the slope, which increases subsequently. Average slopes of the two graphs are different due to difference in the gold film thickness.

In the case of the OT-modified surface, we observed an increase in the slope above 330 K. This is shown in Figure 4A,

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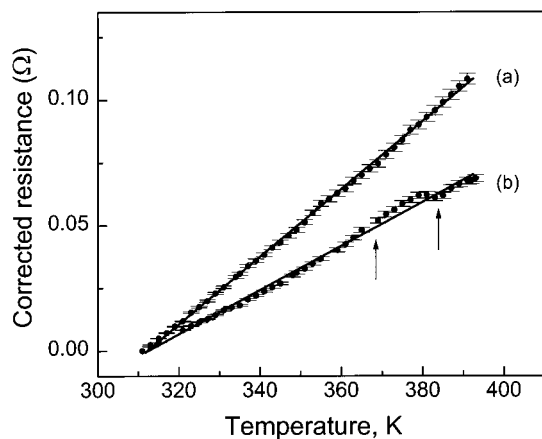
Figure 3. (a) Resistance vs temperature plot of a thin gold film. Note that the resistance changes linearly. (b) Resistance vs temperature plot of ODT monolayer-modified gold film. Corrected resistance refers to $R_T - R_{RT}$, where R_T and R_{RT} are the resistances at temperatures T and room temperature (RT), respectively. The corrected resistance at the start of the experiment has been arbitrarily fixed to zero. The error in the resistance measurements is 2%, and the uncertainty in the temperature is 2 °C.
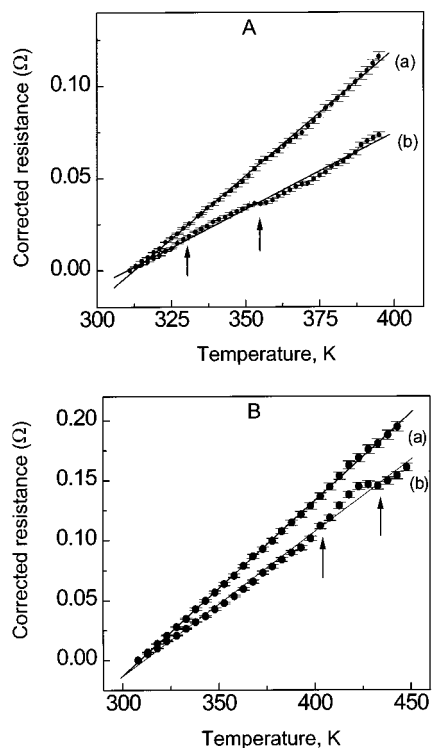

Figure 4. (A) (a) Resistance vs temperature plot of a thin gold film. (b) Resistance vs temperature plot of OT monolayer-modified gold film. (B) (a) Resistance vs temperature plot of a thin gold film. (b) Resistance vs temperature plot of BDMT monolayer-modified gold film. See the caption for Figure 3. Variations in the slope are marked.

where the resistance behavior is again compared with the same bare gold film as in Figure 3. An initial increase in slope is seen around 330 K. Later, a decrease is observed commencing at 355 K. A further decrease is seen at 370 K. In the PT case, no increase in slope is observed, unlike in the case of ODT and OT, but a decrease in the slope is seen which is attributed to the desorption of the monolayer (data not shown). This is because the structure of PT on gold resembles that of a liquid even at room temperature.

Table 1. Comparison of the Reported Phase Transition Temperatures of Alkanethiol Monolayers on Au from the Literature and Transition Temperatures Observed in the Present Study

alkanethiol	phase transition temp (K)	transition temp from present study (K)
$CH_3(CH_2)_2SH$		370[d]
$CH_3(CH_2)_7SH$		~330,[c] 355[d]
$CH_3(CH_2)_{11}SH$	>323[a]	
$CH_3(CH_2)_{13}SH$	>343[a]	
$CH_3(CH_2)_{17}SH$	>350[b]	>360,[c] 385[d]

[a] Data from XRD studies.[8b] [b] Data from RAIRS studies.[12] [c] Phase transition temperatures from the present study. [d] Temperatures corresponding to the onset of desorption of monolayers from the gold surface.

A scanning tunneling microscopic (STM) study by Poirier et al.[20] also suggested that the short-chain thiols (C_4 and C_6) are liquidlike even at room temperature. The phase transition temperatures of alkanethiol monolayers determined by other methods and the transition temperatures seen in resistance measurements are given in Table 1.

The phenomenological model[21] of resistivity increase upon adsorption attributes the effect to nonspecular electron scattering at the metal surface. This model applies to metal films with a thickness less than or comparable to the electron mean free path. Apart from the phenomenological model, the diffuse scattering model developed by Persson and co-workers takes the electronic structure of the interacting system into account (eq 1). The damping rate $1/\tau$ is related to adsorbate density of states at the Fermi energy, $N(E_F)$.

$$1/\tau = (2m\omega_F\Gamma/M)N(E_F)<\sin^2\theta> \qquad (2)$$

where m is the electron mass, $\hbar\omega_F = E_F$, Fermi energy, Γ is the width of the adsorbate density of states, and $<\sin^2\theta>$ is a geometric factor depending on the orbital symmetry of the adsorbate molecular orbital near E_F. This means that increasing adsorbate density of states at E_F increases resistivity. Many of the parameters affecting the damping rate are sensitive to temperature.

Above 360 K, an additional contribution to the increase in slope of the resistance vs temperature curves occurs in the case of the ODT-covered surface. The following two reasons suggest that additional increase in the slope of the resistance can be attributed to the phase transition of the monolayer assembly. (1) The temperature at which this change occurs is around the structural transitions seen in monolayers.[8–12] There is no other process that can occur at this temperature such as the desorption of the monolayer.[9b,c] Reconstruction and modification of the gold thin films are also important to consider, but not significant at this temperature.[22] (2) The temperature at which this change occurs is lower in an OT-covered surface and the change is not observed

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in the PT surface. While the substrate characteristics should be the same in all these monolayers, the only reason attributable is the difference in the extent of order between them. At this point it may be mentioned that a reduction in the lifetime of the adsorbate parallel mode can increase the resistance of the monolayer-covered surface. Around the phase transition temperature (from the solid to liquidlike structural transition), chain untilting occurs and the molecules become orientationally disordered, which increases the damping rate and thereby the lifetime decreases. This is because as the long-range molecular assembly is destroyed, the adsorbates have increased lateral mobility at the substrate surface. Melting the monolayer assembly is the only event that can reduce the lifetime of the lateral vibrational mode in this temperature range. Since the observed transition temperature coincides with the melting temperature of the ODT monolayer and the fact that this temperature is lower in OT and the transition is completely absent in PT support the above suggestion. It could also be argued that as the temperature is increased, it is possible for the adsorbates to occupy sites that contribute to an increased surface resistance. However, such a possibility cannot explain the differences observed between OT and ODT and the lack of any transition in PT. This melting transition observed in SAMs is irreversible, and the features were not reproduced with thermal cycling.[11,12]

The decrease in the slope observed at higher temperature in all three cases is attributed to the commencement of desorption of monolayers from the gold surface. Although complete desorption occurs at higher temperatures ($T > 450$ K),[9b,c] desorption commences above 350 K itself.[12,9b] Our own studies using SERS also indicate that the monolayer desorption commences above 350 K.[18]

The resistance vs temperature plot for the BDMT monolayers is shown in Figure 4B. The data are compared with that of a pure gold film. In our earlier SERS study,[23] we found that this molecule binds to the gold surface with one thiol group and the other was free at the surface, whereas on the silver surface, the molecule binds to the surface with both the sulfur atoms. This makes the benzene ring perpendicular to the surface in the former and parallel in the later. The molecule on the gold surface at high temperature ($\sim$373 K) loses its free thiol proton at the surface and starts falling on the surface at around 370 K; i.e., the benzene ring approaches a near-parallel geometry. The resistance of the BDMT-covered gold surface (Figure 4B) increases linearly with temperature up to 390 K. It then deviates from the linear behavior and the slope increases up to 423 K. We attribute the change in slope to the structural changes in the monolayer. It appears that this change is manifested in SERS much earlier than in resistance. The falling down of the molecule makes the benzene ring and the free sulfur present at the monolayer surface approach closer to the gold surface. This structural change may also result in an increased adsorbate density of states at E_F. Increased density could also have a contribution from the increased π interaction. It may be noted that the extent of change in resistance observed is different in alkanethiol monolayers and BDMT. Thus, the structural transitions in alkanethiol and BDMT monolayers are manifested in resistance for two possibly independent reasons.

CONCLUSIONS

This study shows that simple four-probe resistance measurements manifest fluctuations at temperatures close to the phase changes and desorptions of alkanethiol monolayers self-assembled on gold surfaces. The observations presented here clearly indicate that around two different temperatures, the monolayer-modified gold surfaces show distinct changes in the slope of the resistance vs temperature plot. One is due to phase transition (order−disorder transition) manifested as an increase in the slope of the resistance vs temperature plot compared to the linear behavior of the pure gold surface, and the other is due to the desorption of monolayers from the surface manifested as a decrease in slope at higher temperatures. Adsorbate geometry effects are also seen in resistance, as observed in the case of a BDMT monolayer.

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