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Surface resistance investigations of the exchange of 3D monolayers with molecules self-assembled on planar gold surfaces

M. Venkataramanan, T. Pradeep [*]

Department of Chemistry and Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Chennai – 600 036, India

Abstract

Simple four probe resistance measurements have been used to study the ligand exchange between monolayer protected clusters of Au and Ag with dithiol monolayers on planar gold surfaces. The decrease in in-plane resistance upon exposure of functionalized dithiol monolayer covered gold surfaces to monolayer protected cluster solutions is attributed to the attachment of free thiol groups of the monolayers on the gold surfaces to the clusters. This linking of clusters to monolayers results in screening of electron–adsorbate vibration interaction causing a decrease in resistance. There can also be additional factors determining the observed changes. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Self-assembled monolayers (SAMs) [1–4] have become model surfaces to study many interesting and technologically important phenomena such as wetting [5], molecular recognition [6], adhesion [7], electron transfer [8], etc. These well organized crystalline like assemblies have been used to support metal particles on surfaces in order to understand the weak electronic coupling between the particles and the underlying substrate [9]. Attachment of semiconductor nanoparticles of CdS [10,11], CdSe [12] and PdS [13] onto SAM surfaces has been reported. Arrangement of these nanoparticles on solid supports is necessary in the construction of electronic devices such as SET (single electron transistor) [14].

Andres et al., [15–17] have studied the single electron tunnelling of Au clusters tethered on α, α'-xylyldithiol monolayer by scanning tunnelling microscopy (STM). They observed a Coulomb staircase behavior at room temperature when an STM tip was positioned over a cluster bonded to a dithiol SAM. This and other studies [10–12] showed that the metal clusters can be covalently bonded to one or more sulfur atoms on the monolayer surface. By this process, the clusters are immobilized on the surface. A resonance Raman spectroscopic study showed that clusters on the monolayer surface do not coagulate with the neighbouring ones [10]. As a result, SAMs provide a model surface to study the properties of single clusters.

Murray's group has observed ligand place exchange upon mixing capped clusters with ω-functionalized thiols in solution [18–21]. They found that some of the monoalyers on the cluster surface are

[*] Corresponding author. Fax: +91-44-235-0509; e-mail: pradeep@acer.iitm.ernet.in

replaced by thiols in solution. Recently Chen and Murray [21] have observed ligand place exchange by exposing monolayer capped gold clusters to dithiol monolayers on Au electrodes. They have studied the double layer capacitance charging of nanometer sized monolayer protected gold clusters anchored to a macroscopic gold electrode by differential pulse voltammetry (DPV), ac impedance and charge transfer resistance.

Zhang et al. [22], have shown that a simple in-plane resistivity method can be used to understand the chemisorption and chemical reaction effects at liquid-solid interfaces. We also used the same method to study the phase transition and desorption of self-assembled monolayers from planar gold surfaces [23]. In this paper, we study change in the in-plane resistance of a SAM modified thin Au film upon exposure to a solution of octanethiol capped Au and Ag clusters. We observed a decrease in the resistance of Au films modified by 1,6-hexanedithiol (HDT) and 1,4-benzenedimethanethiol (BDMT) monolayers when they were exposed to octanethiol capped gold (AuOT) and silver (AgOT) clusters. The observed decrease may be due to the exchange of one (or) more octane thiol monolayers on the cluster surface with the free thiol groups of the dithiol monolayer anchored on the gold surface. This makes the clusters immobilized at the surface and attach directly to the underlying Au surface. This attachment may result in the screening of electron–vibration interaction by the metallic particles causing a decrease in resistance; additional factors may also be responsible for the observed phenomena. The observed slow decrease in resistance for the HDT monolayers compared to BDMT monolayers when exposed to the same cluster solutions is attributed to the kinetics of ligand exchange.

2. Experimental section

The gold films 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 ultra pure water. These plates were sonicated for 1 h in water. They were then 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 the voltage were kept at 4 mA and 1.5 kV, respectively. Initially titanium was coated for 10 m which was followed by gold for 30 m. The gold and titanium used for coating were 99.8% pure. The expected film thickness under these conditions is 500 Å. Grain boundaries and point defects in the films were removed by annealing them at 600 K for roughly 10 h [24].

The flow cell for resistivity 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 sides 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 four gold wires. In-plane resistance measurements were done by keeping the gold plate above the cell with a viton 'O'-ring spacer as the liquid seal. The gold plate was pressed such that it was in contact with the four gold wires. A schematic of the experimental set-up is given elsewhere [23].

Monolayers were prepared by exposing 1 mM solution of the corresponding dithiols 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 cc/h. Once the films were formed (in the cell, 12 hours of continuous exposure), they were repeatedly washed with ethanol and dried with argon in-situ. After drying, the cluster solution was passed through another silicone tube to the same set-up for 1 hour. The resistance was measured simultaneously by connecting the four gold wires to a Keithley model 2001 multimeter which was interfaced with a computer. The viton 'O'-ring was covered with a teflon tape to protect the thiol and the cluster solutions from possible contamination.

The clusters (AgOT and AuOT) were prepared by the procedure originally developed by Brust et al. [25]. For the ligand place exchange reaction, 0.05 g of the cluster in 10 ml toluene was mixed with 0.05 g of BDMT in 10 ml toluene. The mixture was stirred vigorously for 24 h. The product was washed several times in methanol and acetone to

remove excess or free thiol molecules. The insoluble nature of the exchanged product in any organic solvent is a clear indication of complete exchange of BDMT in place of OT on the cluster surface.

The infrared spectra were collected in the transmission mode with a Bruker IFS 66v FT-IR spectrometer. A KBr pellet was prepared by mixing approximately 1 mg of the sample with 1 g potassium bromide. The spectra acquired were averages of 200 scans, which were background subtracted automatically.

3. Results and discussion

Fig. 1A shows the resistance vs time plot of the BDMT monolayer on Au surface exposed to octanethiol capped silver clusters. The resistance of the gold film started decreasing immediately when the monolayers were exposed to the cluster solutions. The resistance reaches a minimum value within the first 20 minutes and thereafter changes only to a negligible extent. Fig. 1B displays the decrease in resistance when AgOT clusters were exposed to HDT monolayers on the Au surface. Unlike the BDMT case, the decrease in resistance is slower and continued up to 40 m.

Fig. 2 displays a comparison of the FTIR spectra of BDMT solid, AgOT cluster and BDMT exchanged with AgOT cluster for 24 h. The peak observed at 2552 cm^{-1} corresponding to S–H stretching (Fig. 2a) disappears upon adsorption on the cluster surface (i.e. absent for the exchanged product, Fig. 2c). The peak at 669 cm^{-1} of the BDMT solid corresponding to the C–S stretching is downshifted to 676 cm^{-1} in the exchanged sample. The shift is due to adsorption of BDMT molecules on the cluster surface [26]. The bands at 763, 1228, 1417, and 1509 cm^{-1} observed for the exchanged product are assigned, respectively to the ring breathing, methylene wagging, methylene scissoring and ring C–C deformation modes. The peaks appearing at 2922 and 2952 cm^{-1} are due to the methylene symmetric and antisymmetric vibrations, respectively. The aromatic C–H bands appear at 3018 and 3045 cm^{-1}.

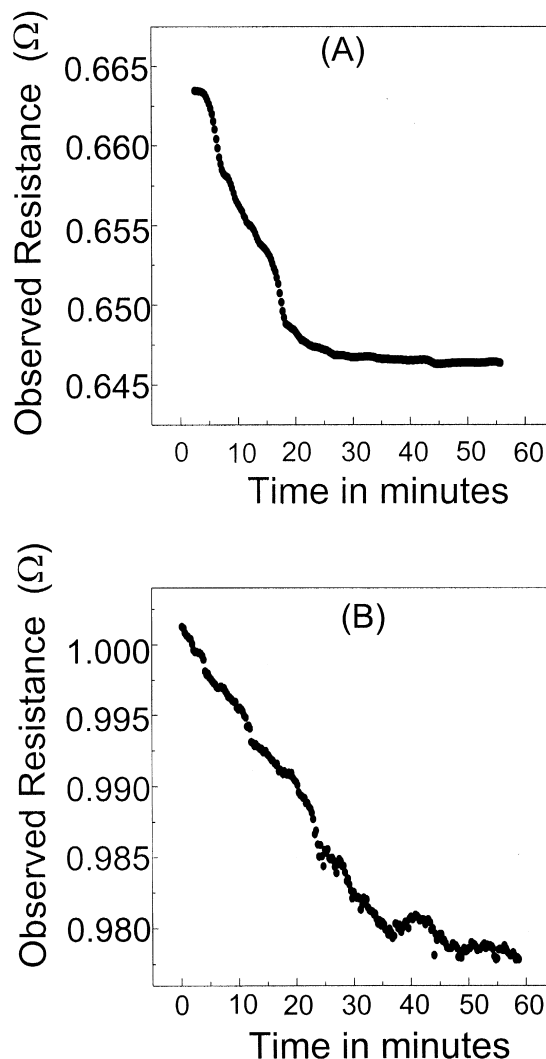The FTIR spectrum for AgOT is shown in Fig. 2b. Bands appearing at 1463, 1400 and 1194

Fig. 1. (A) Resistance vs time plot for BDMT monolayer covered gold upon exposure to octanethiol capped silver clusters. (B) Resistance vs time plot for HDT monolayer covered gold upon exposure to octanethiol capped silver clusters. The resistances are not corrected for the contributions due to lead wires, contacts, etc.

cm^{-1} correspond to methylene scissoring, wagging and rocking modes, respectively [27]. The peaks at 1118 and 1068 cm^{-1} are assigned to $(C–C)_T$ and $(C–C)_G$ stretching modes, respectively. The peaks observed at high frequency region correspond to methylene stretching regions. The presence of characteristic BDMT features at 1509, 1228 and 1417 cm^{-1} and the absence of OT features at 1118 and 1463 cm^{-1} in the BDMT exchanged AgOT spec-
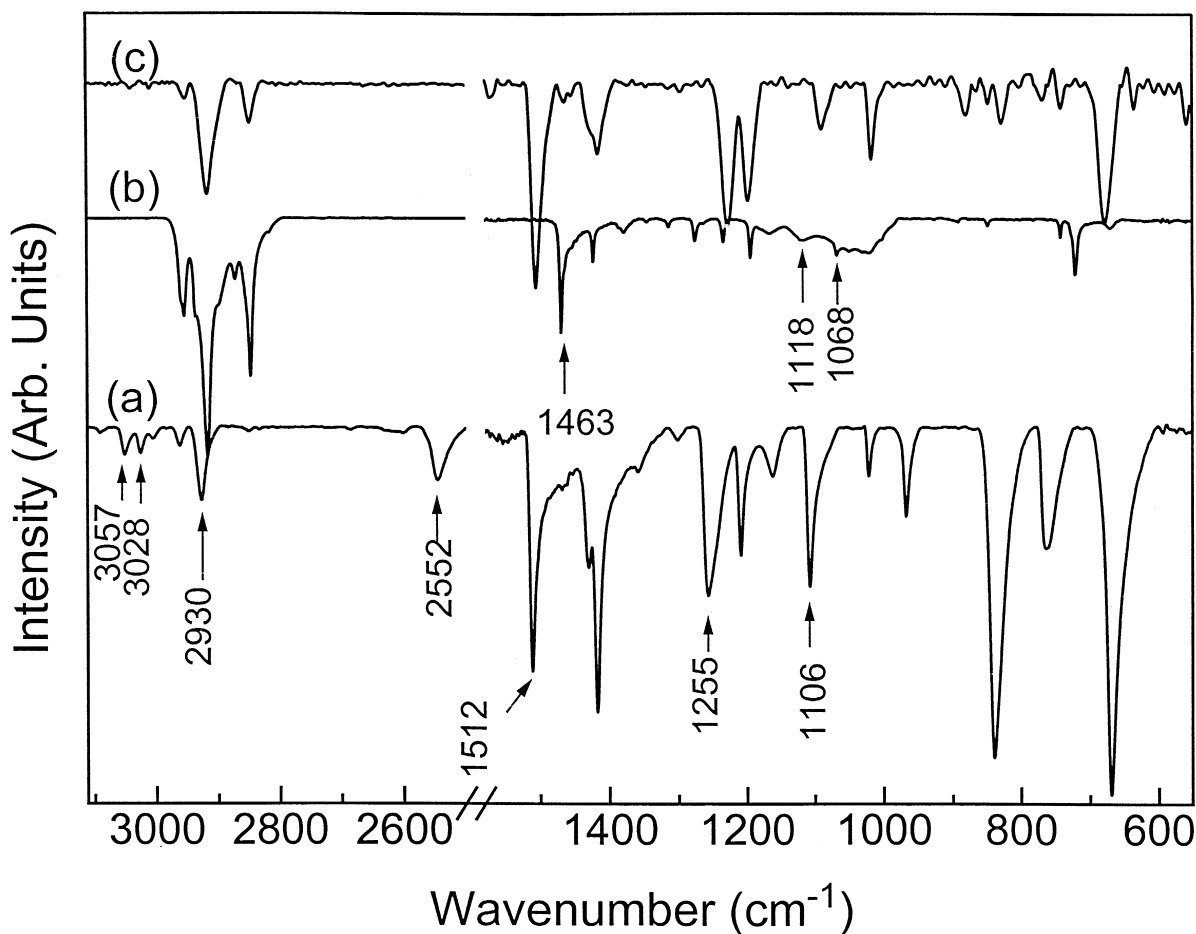
Fig. 2. FTIR spectra of (a) Solid BDMT, (b) AgOT cluster, and (c) BDMT exchanged with AgOT cluster for 24 h. The characteristic BDMT peaks are marked. Note the presence of BDMT features for the exchanged product.

trum clearly indicates the exchange of BDMT molecules in place of OT. This kind of ligand place exchange reactions have been reported earlier [18–20].

Fig. 3A shows the decrease in resistance of the BDMT covered Au film upon exposure to AuOT cluster solution. The observation is similar to that for AgOT exposed to BDMT monolayers. The FTIR spectrum of AuOT exchanged with BDMT in toluene for 24 h is shown in Fig. 3B. The presence of characteristic BDMT peaks indicates the exchange of BDMT molecules in place of OT. Exchange of HDT with 1-hexanethiolate protected gold clusters has been reported earlier [28].

The resistance of a thin gold film increases when exposed to thiol solutions. The increase in resistance

is attributed to the effect of dipoles on the diffuse scattering of charge carriers on the surface of the metal [22]. The increase in resistance is abrupt when the film was exposed to alkane thiols, whereas the resistance increases to $3/4^{th}$ of the alkane thiol value when exposed to aromatic thiols [22,23]. This difference was attributed to the difference in the extent of electronic interaction between aliphatic and aromatic thiols with the gold surface [22].

As observed by Chen and Murray, [21] we expect the free thiol groups (one or more) on the monolayer surface to replace the octane thiol groups on the cluster and thereby get bound to the cluster. This anchors clusters on the surface and the cluster core is directly bridged to the underlying gold substrate through dithiol moieties. Earlier reports also show
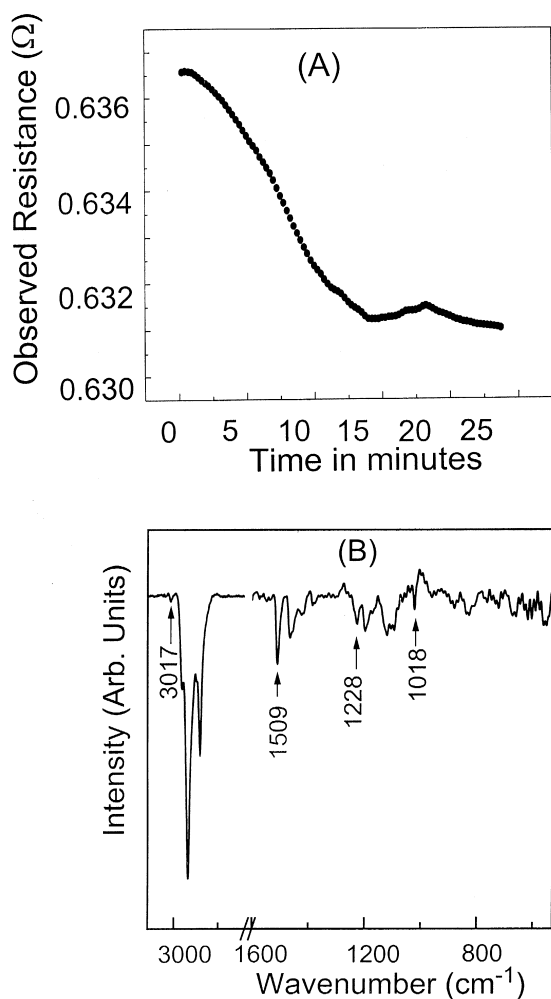
Fig. 3. (A) Resistance vs time plot for BDMT monolayer covered gold upon exposure to octanethiol capped gold clusters. The resistances have not been corrected for the contributions due to lead wires, contacts, etc. (B) FTIR spectrum of AuOT cluster after exchange with BDMT solution for 24 h. Important BDMT peaks are marked.

that clusters can be attached and immobilized on the surface of the monolayer [10–13]. This kind of exchange reactions are also reported for self-assembled monolayers on 2D surfaces [8,29].

The increase or decrease in surface resistivity can be explained by the following Perrson equation,

$$1/\tau = \left(n^2 e^2 / M\right) d\Delta \rho / n_a \qquad (1)$$

where n and e are electron number density and charge, d is the film thickness, $\Delta \rho$ is change in resistivity, M is the adsorbate mass, n_a is adsorbate number density and τ is the lifetime of the parallel vibrational motion of the adsorbate due to the excitation of electron–hole pairs [30–32]. The term $1/\tau$ (damping rate) in Eq. (1) is also related to $N(E_F)$ which is the adsorbate density of states at the Fermi energy by the following Newns–Anderson model [31,32],

$$1/\tau = \left(2m\omega_F \Gamma / M\right) N(E_F) \langle \sin^2 \theta \rangle \qquad (2)$$

where m is the electron mass, $\hbar \omega_F = E_F$, Fermi energy, Γ is the width of the adsorbate density of states and $\langle \sin^2 \theta \rangle$ is a geometric factor depending on the orbital symmetry of the adsorbate molecular orbital near E_F and $N(E_F)$ is the adsorbate density of states at the Fermi energy.

The observed decrease in resistance may be explained by the following reasons. Binding of the cluster to the monolayer may increase the lifetime of the parallel vibration of the adsorbates, which decreases the damping rate, and thereby the resistivity decreases (compared to the parent monolayer). Note that the adsorbate has to move along with the heavy cluster bound to it. As a result of exchange of monolayers with clusters, the adsorbate vibrational density of states may increase (compared to the parent monolayer) due to the net increase in adsorbate mass and consequent decrease in the vibrational frequencies. It is unlikely that the electronic density of states would decrease greatly because the particles are protected with the hydrocarbon monolayer. However, the interaction of the electrons in the gold film with the adsorbate vibrations can be affected by the presence of the metallic cluster. Since terms in Eq. (2) (such as M) are not going to produce large change in resistance, we suggest that the screening effect of the metal particles has a dominant effect in the observed decrease in resistance.

The faster decrease in resistance when BDMT monolayers were exposed to cluster solutions compared to HDT monolayers may be attributed to the kinetics of exchange. Although both are thiols, there can be structural reasons, contributing to the exchange chemistry.

4. Conclusions

In this Letter we show that the simple four probe resistance method can be used to study the ligand place exchange reactions when capped clusters are exposed to self-assembled monolayers of dithiols on planar Au surfaces. The resistance of the underlying gold surface decreases when octane thiol capped clusters are exposed to dithiol monolayers. This decrease is attributed to the exchange of octanethiol molecules (one or more) with the dithiol monolayers on the Au surface. This exchange of monolayers with clusters appears to affect the interaction of the electrons in the film with the adsorbate vibrations as a result of the screening effect of the metallic particles. There can be weaker effects due to reduced damping rate, change in adsorbate mass, etc. Although factors such as the extent of coverage, number of molecules involved in the exchange, the chemical nature of the species which left the surface, etc., are important in the phenomenon, the present experiments do not provide details on them.

Acknowledgements

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