CHAPTER 4

Effect of surface pretreatment on the adsorption properties of alkanethiols:

4.0 Introduction:

Long chain alkanethiols chemisorb strongly and form highly ordered and stable self assembled monolayers on different metal surfaces such as copper [1-6], silver [7-8] and gold [9-13]. Understanding of the various factors that govern the formation, structure and properties of self assembled monolayers is important in the study of various interfacial phenomena. Because of their utility in manipulating interfacial structure SAMs have been used as molecular probes of diverse interfacial phenomena such as ionic and molecular recognition, protein adsorption, wetting, adhesion, tribology etc. The well ordered and close packed nature of the monolayers make them ideal for testing different surface analytical techniques that are sensitive to molecular properties.

A gold substrate can be coated with an organised monolayer simply by immersing the electrode in a dilute solution of alkanethiol or sulphide. Efforts to achieve the most blocking or highly oriented monolayer on a gold substrate have led to a consideration of several factors in the self assembly process, namely, substrate morphology, cleaning, alkanethiol purity, deposition solvent, deposition solution concentration and deposition time. The well ordered close packed nature of many of these films makes them ideal model systems for testing new surface techniques that are sensitive to molecular properties. They also offer an attractive means of building chemical functionality into an interface, with the eventual goal of defining and controlling reactivity patterns. One of the important properties of an alkanethiol monolayer is its binding to an electrode surface and the inhibiting behaviour of the resulting monolayer film to electron transfer reaction [14-17]. An important attribute of these films that has proved difficult to characterise is the defect sites, many potential applications of self assembled monolayers require that they be extremely free of defects. Yet there are no reliable diagnostic tests to determine what the nature and density of defect sites are, what cause them and how to prevent them. A small number of defect sites can have a major impact on the behaviour of the monolayer. One of the macroscopic properties of a monolayer that correlates with defectiveness is permeability; monolayers that are more permeable to small molecules eg. solvent, ions and electroactive solutes are more defective than monolayers that are not permeable to such species. For alkanethiol SAMs on noble metal surfaces, monolayer permeabiliy may be a function of many factors such as structure of the molecule, dipping time in the coating solution, the nature of the solvent, the nature of the substrate onto which the monolayer is coated, pretreatment applied to the substrate prior to monolayer deposition etc. A lot of research is involved in searching for new ways to prepare monolayers in which the defect density is low.

The first choice in terms of morphology of substrate is polycrystalline versus single crystal substrate. If the substrate is a single crystal, then a particular face can be selected. Most of the work has been done on evaporated or sputtered gold films on cleaved mica, polished single crystal silicon or glass. The gold films exhibit strong Au (111) character when deposited. We were interested in exploring other alternative procedures for preparing polycrystalline gold substrates prior to monolayer formation. While a well defined single crystal face is important for many surface analytical methods (e.g. electron diffraction, He atom scattering, scanning tunneling microscopy etc.) there is no consistent evidence to show that pinhole free SAMs require a single crystal surface. The presence of impurities, grain boundaries or large steps between atomically smooth planes may have more effect on the electrochemical properties of the SAM coated electrode than the degree of crystallinity.

Creager et al. [18] reported on the defectiveness of the monolayers of alkanethiols formed on polycrystalline gold pretreated by oxidative chemical etching in aqua regia. They characterised the gold substrates by lead underpotential deposition, gold oxide stripping, scanning electron microscopy and scanning tunneling microscopy. The quality of a monolayer is judged by its ability to inhibit the electron transfer between the underlying gold electrode and a redox active molecule present in the contacting solution. They also monitored the exchange of chemisorbed alkanethiols, present after a first coating step, with other "tagged alkanethiol molecules from solution. The tagged molecules had a redox active ferrocene moiety linked to an alkanethiol to facilitate the quantitative exchange reaction. They find that bulk polycrystalline gold electrodes when properly treated are suitable substrates for supporting self assembled monolayers of alkanethiols and are in many ways superior to the more conventional evaporated gold films. Pretreatment of bulk gold by etching with aqua regia produces surfaces that are visibly rough but very smooth on the microscopic scale. Defect densities are lower in monolayers on etched bulk gold than in similar monolayers on evaporated gold thin films even when the evaporated films have been annealed prior to monolayer formation. An evaporated gold surface though macroscopically smooth was found to be microscopically rougher than the chemically etched surface. They concluded that microscopic roughness and the presence of crystal grain boundaries are the key factors in determining how substrate morphology affects the properties of self assembled monolayers. SAMs on polycrystalline gold electrodes were found to be superior to SAMs formed on evaporated gold films.

Creager et.al. [19] also studied the effect of surface treatment [alumina polishing $(0.3\mu m)$ and chemical etching] on the redox kinetics for ferrocene groups immobilised in mixed self assembled alkanethiolate monolayers (ferrocene carboxamide + 16-mercaptohuxadecanol) on gold electrode. They find that the background current for the monolayer on the polished electrode is much higher

than that of the etched electrode. They postulated that the increasing background currents at the alkanethiol coated polished gold electrodes reflect the fact that the monolayers on such electrodes are defective and therefore permeable to solvent and/or ions from the contacting electrolyte solution. This enhanced permeability increases the total capacitance of the interface. Monolayers on etched electrodes are found to be much less permeable and exhibit smaller capacitances. They also found that the electron transfer kinetics for ferrocene groups in the two types of monolayers are nearly identical, despite the obvious differences in the monolayer permeability and therefore defectiveness. This was valid for all the sweep rates examined. They speculated that the surface of the polished gold electrode could be heterogeneous, consisting of some regions in which the ferrocene groups are held away from the electrode in the more or less ordered alkanethiolate based monolayers, and other regions in which the surface is free of any ferrocene containing material. If the latter regions are relatively more accessible to solvent and /or electrolyte, then the overall interfacial capacitance of the coated electrode would be higher than that of a similarly coated electrode without such regions. The degree to which a monolayer is permeable would depend on the relative areas of these two types of regions. They argue that the exposed regions would form on the polished electrode but not on the chemically etched electrode. This could be because strongly adsorbed surface contaminants are present after the polishing step that are not easily displaced by the thiols but that are removed by the etching step.

Guo et al. [20] examined the influence of gold surface topography and surface pretreatment on the defect structure of alkanethiol monolayers on gold. The topography of gold films evaporated on mica was controlled by varying the mica substrate temperature. Gold films evaporated onto heated mica substrates are found to be microscopically smooth, containing large atomically flat terraced areas. Lowering of substrate temperature during gold evaporation leads to increasingly rougher gold films. The blocking characteristics wcrc investigated by cyclic voltammetry and scanning tunneling microscopy. They find that the SAMs become significantly less blocking as the mica substrate temperature during gold evaporation is increased and consequently as the gold surface topography becomes smoother. They infer that adventitious contamination during evaporation result in defect sites (depressions) which are concentrated at grain boundaries. These sites may serve as the loci for pinholes in the self assembled monolayer. This is in conflict with the conclusion of Creager et al. that the microscopic roughness which is present on a surface which may appear smooth at the macroscopic level is responsible for defect formation.

To resolve this issue and to understand the exact role of surface morphology in influencing the blocking characteristics we thought it worthwhile to carry out a systematic study of the effect of substrate roughness and surface pretreatment on the defect properties of alkanethiol monolayers on gold, silver and copper [21,22]. We investigate the structural stability of octadecanethiol monolayer formed on polycrystalline gold subjected to the following kind of pretreatments:

- 1. Mechanical polishing
- 2. Chemical etching
- 3. Electropolishing
- 4. Electrochemical formation of surface oxide
- 5. Evaporated gold on mica

We intentionally introduced controlled roughness on the polycrystalline substrates by mechanical polishing and examined the role of surface roughness on defect formation in the monolayer. The advantage of this approach is that not only can one control the extent of roughness created on the surface, but also vary the same to study if there is any correlation between the substrate roughness and defect formation in the monolayer. We have used cyclic voltammetry to study the defect formation and structural stability while the role of surface morphology was examined by scanning tunneling microscopy .We have compared these results with monolayers formed on chemically etched, electropolished surfaces and electrochemical oxide formed surfaces.

We study the effect of mechanical polishing by gradually varying the particle size of the polishing materials. The topography of the substrate is thus changed in a controlled manner during each treatment. The corresponding roughness factor is determined for gold in each case by cyclic voltammetry [23]. The blocking nature of the self assembled monolayer on the metal electrodes is determined by the cyclic voltammetry of the respective metal oxidation and reduction reaction in alkaline media. We have used this method of characterising the film because:

- 1. It is reported in literature [24] that the oxide stripping current affords a quick assessment of the area fraction of the pinholes since the oxidation of the metal can only occur if the redox species (hydroxyl ions in this case) can reach the electrode surface, through the pinholes. Hence the charge measured from the area under the peak is indicative of blocking behaviour of the monolayer.
- 2. All the three metals studied exhibit well defined and reproducible oxidationreduction peaks in alkaline media.

4.1 Experimental:

4.1.1 Electrode preparation:

Copper, silver and gold were of > 99.9 % purity and used as metal strips. The electrode is designed in such a way that one end of the metal strip could be attached to the split end of a gold plated brass rod with screws. A well defined region of the other end of the electrode is exposed to the electrolyte, the remaining portion being well insulated with Parafilm [A self sealing inert thermoplastic (American National Can)] and then with Teflon. The geometric areas of gold,

silver and copper were I cm^2 respectively. Before each experiment, the actual geometric areas of the electrodes were measured and it generally ranged within 5 % of the above values.

4.1.2 Electrode treatment:

a) Mechanical polishing:

Each metal surface is hand polished with emery papers of grades 800,1000 and 1500. The general metallographic procedure is followed during the polishing sequence. As per ASTM specifications, the average particle sizes of the above papers are 17 pm, 13 μ m and 9 μ m respectively. The electrodes after polishing are rinsed in milli pore water, sonicated, dried and immediately immersed in a solution of 1mM octadecanethiol (Aldrich) prepared in absolute ethanol for 30 minutes. For preparing alumina treated surface, the metal surface after polishing successively with the above three grades of emery paper was further polished on a micro cloth having a slurry of 1, 0.3 and 0.05 μ m alumina powder (Buehler make) successively.

b) Aqua regia and nitric acid etching:

The gold strip after polishing with alumina powder was etched in concentrated aqua regia solution (3:1 HCl and HNO₃) for one minute before immersion into octadecanethiol solution. Silver and copper were etched in 8N HNO₃ for one minute before immersion.

c) Electropolishing:

Gold electropolishing [25] was done in a solution containing 4gm dm'' KCN and 7gmdm⁻³ of Potassium sodium tartarate. The current density was maintained at I A cm⁻² for one minute. Copper electrode was electropolished [25] in a solution containing 35 ml of 45N phosphoric acid and 9 ml of n-butanol.

Stainless steel was used as the cathode. The current density was maintained at 1.5 A cm⁻² for one minute.

d) Electrochemical surface oxide formation:

The potential of gold, silver and copper electrodes were kept at potentials corresponding to their respective oxide formation, viz. at values of 0.3V, 0.4V and -0.2V versus $H_g l Hg_2 SO_4 (sat Na_2 SO_4)$ reference electrode. In the case of gold and copper the oxidation was carried out for 5 minutes, where as for silver it was for 1 minute. This ensures the formation of an oxide film on the electrode surface. The electrode is then taken out at that potential rinsed in millipore water, air dried after which it is dipped immediately in octadecanethiol solution for 30 minutes.

4.1.3 Electrochemical studies:

A conventional three electrode electrochemical cell was used. The counter electrode was a platinum electrode of sufficiently large surface area. All the potentials were measured against $Hg/Hg_2SO_4(satNa_2SO_4)$ reference electrode. Additional inlets were provided at the top of the cell, which was made of Borosil glass with teflon cap for the passage of nitrogen gas. Before each experiment the cell was completely deaerated by passing nitrogen gas. During the experiment a blanket of nitrogen gas was maintained on top of the solution.

Cyclic voltammetry was carried out using an EG&G potentiostat (Model 263A) interfaced to a PC through a GPIB card (National Instruments). Charge measurements were carried out from the first scan of the cyclic voltammogram in each case. The potential ranges and scan rates are shown in the following table.

METAL	POTENTIAL RANGE	SCAN RATE
GOLD	-1.15 V to 0.3 V	100 mV sec ⁻¹
SILVER	-0.6 V to 0.4 V	20 mV sec ⁻¹
COPPER	-1.5 V to -0.2 V	20 mV sec ⁻¹

The real surface area of gold was determined by cyclic voltammetry using the cathodic stripping peak of gold in 0.5 N Sulphuric acid obtained at a scan rate of 100 mV sec⁻¹ and scan range of -0.610V to 1V versus $Hg/Hg_2SO_4(satNa_2SO_4)$ electrode. The electrolyte used was 0.1 M NaOH solution prepared in millipore water.

Electrochemical impedance spectroscopy was performed using an EG&G potentiostat (Model 263A) along with a lock in amplifier (Stanford Research Systems Model SR830). A pure sine wave of 4mV amplitude was derived from the lock- in amplifier for application to the cell. The current output was in turn connected to the lock- in amplifier input. Impedance was measured over a frequency range of 1 Hz to 30kHz.

4.1.4 Scanning tunneling microscope studies:

STM studies were carried out in air on gold surface after different surface treatments before and after the formation of monolayers. The gold samples were immersed in 1mM octadecanethiol solution for 30 minutes, washed with absolute ethanol, dried and immediately mounted on the STM sample holder. The images were taken within 30 minutes after this process. A home made STM [26] described in chapter-3 was used. The measurement was carried out at constant current mode. This was calibrated by imaging with a highly oriented pyrolytic graphite (HOPG) surface before the experiments. The images shown are of raw

data without any filtering. However the plane tilt correction was carried out. The images are displayed using the IDL (5.02) software (Research Systems Inc. USA) and the roughness measurements were carried out using SPIP software developed by the Danish Institute of fundamental metrology. Electrochemically etched tungsten tip was used as a probe. The tunneling current for imaging the bare surface was 1nA at a bias voltage of 100 mV, while for the alkanethiol adsorbed surface the tunneling current 200pA at the same bias voltage. STM imaging was carried out at different regions of the surface and at several scan ranges to verify the overall reproducibility of the surface features.

4.1.5 Optical microscopic images:

Optical microscopic images were acquired for gold surface with different pretreatments using a Leitz microscope fitted with a 35mm camera.

Results and Discussion:

4.2 Cyclic voltammetric studies:

Figures 1(A), 2(A) and 3(A) show the cyclic voltammograms of bare gold, silver and copper in 0.1 M NaOH solution. The cyclic voltammograms were taken after 15 minutes of immersion and at room temperature. The cyclic voltammogram of copper in 0.1 M NaOH solution shows three anodic and two cathodic peaks. It is reported that the first anodic peak corresponds to the oxidation of Cu to Cu₂O monolayer formation. The second and third peaks have been ascribed to multilayer formation of CuO in parallel pathways viz, oxidation of Cu₂O to CuO and another directly from Cu by two electron transfer [27]. In the reverse scan during cathodic reduction the fourth peak corresponds to the cathodic reduction of CuO to Cu₂O while the fifth peak is due to the reduction of Cu₂O to Cu.

The cyclic voltammogram of silver in 0.1 M NaOH shows the presence of two prominent anodic and cathodic peaks corresponding to the formation of Ag_2O

Legend for figures:

Potentials are referred with respect to Hg/Hg_2SO_4 (sat Na_2SO_4) reference electrode.

Figure 1: Cyclic voltammograms of Gold in 0.1 M NaOH

- (A) Bare Electrode (without dipping in octadecanethiol).
- (B) After aqua regia treatment and 30 minutes dip in 1mM octadecanethiol.
- (C) After electropolishing and 30 minutes dip in 1mM octadecanethiol.
- (D) After holding at a potential of 0.3 V in 0.1 N NaOH for 5 minutes to form oxide and later dipping in 1mM octadecanethiol for 30 minutes.
- (E) After treating with 800 grade emery and 30 minutes dip in 1mM octadecanethiol.
- (F) After treating with 1000 grade emery and 30 minutes dip in 1mM octadecanethiol.
- (G) After treating with 1500 grade emery and 30 minutes dip in 1mM octadecanethiol.
- (H) After treating with 0.05 µm alumina and 30 minutes dip in 1mM octadecanethiol.

Figure 2: Cyclic voltammograms of Silver in 0.1 M NaOH

- (A) Bare Electrode (without dipping in octadecanethiol).
- (B) After nitric acid treatment and 30 minutes dip in 1mM octadecanethiol.
- (C) After holding at a potential of 0.4 V in 0.1 N NaOH for 1 minute to form oxide and later dipping in 1mM octadecanethiol for 30 minutes.
- (D) After treating with 800 grade emery and 30 minutes dip in 1mM octadecanethiol.
- (E) After treating with 1000 grade emery and 30 minutes dip in 1mM octadecanethiol.
- (F) After treating with 1500 grade emery and 30 minutes dip in 1mM octadecanethiol.
- (G) After treating with 0.05 µm alumina and 30 minutes dip in 1mM octadecanethiol.

Figure 3: Cyclic voltammogram of Copper in 0.1 N NaOH

- (A) Bare Electrode (without dipping in octadecanethiol).
- (B) After nitric acid treatment and 30 minutes dip in 1mM octadecanethiol.
- (C) After electropolishing and 30 minutes dip in 1mM octadecanethiol.
- (D) After holding at a potential of 0.2 V in 0.1 N NaOH for 5 minutes to form oxide and later dipping in 1mM octadecanethiol for 30 minutes.
- (E) After treating with 800 grade emery and 30 minutes dip in 1mM octadecanethiol.
- (F) After treating with 1000 grade emery and 30 minutes dip in 1mM octadecanethiol.
- (G) After treating with 1500 grade emery and 30 minutes dip in 1mM octadecanethiol
- (H) After treating with 0.05µm alumina and 30 minutes dip in 1mM octadecanethiol.



Figure 1





Figure 2









and AgO [28-29]. In the case of gold there is a single anodic peak corresponding to the formation of a monolayer of oxygen atoms on the polycrystalline gold surface [30]. During the cathodic scan the peak corresponds to the stripping of adsorbed oxygen.

4.3 Charge measurement studies:

Figures 1 (B-H), 2 (B-G) and 3(B-H) show the cyclic voltammograms of octadecanethiol modified gold, silver and copper electrodes in 0.1 M NaOH for different surface treatments and roughness. There is a marked decrease in the peak heights in all the cases *vis-a-vis* the respective bare electrode which obviously is due to the physical barrier formed by the octadecanethiol monolayer that inhibits the electron transfer reaction. It can also be seen that in the case of silver and copper the anodic peaks are less prominent and rather drawn out than the cathodic peaks after alkanethiol adsorption. These observations show that there is a change in the nature of oxide formation and oxygen chemisorption on the metal covered with octadecanethiol.

Measurement of charge involved in the redox reaction, by integrating the voltammetric peaks provide an estimate of the extent of electrochemical reaction taking place on the surface. Table 1 shows the charges measured for different surface treatments after octadecanethiol adsorption, by integrating both the cathodic peaks in the case of Cu and Ag and the only cathodic peak in the case of Au. The blank values (without alkanethiol adsorption) are shown only for alumina polished surfaces for comparison.

Table 1

Cathodic charges (in mC cm⁻²) measured from the CV's for the blank electrode (alumina polished and without thiol adsorption) and surfaces subjected to different pre-treatments followed by alkanethiol adsorption

PRE-TREATMENT*	GOLD	SILVER	COPPER
BLANK (Thiol free)	0.696	11.77	8.751
800 EMERY (17µm)	0.018	0.661	0.36
1000 EMERY (13µm)	0.018	1.13	1.55
1500 EMERY (9µm)	0.049	4.25	2.13
ALUMINA (0.05µm)	0.148	6.91	3.76
CHEMICAL ETCH	0.00034	0.175	0.492
ELECTROPOLISHING	0.0020		2.200
OXIDE FORMATION	0.032	2.465	1.220
EVAPORATED	0.0295		

* The values given in the parenthesis are the particle sizes of the abrasives used.

We have determined the fractional coverage of the adsorption of octadecanethiol onto gold, silver and copper using the integrated charge values. Though this is only an indirect and semi quantitative method, it provides a quick and convenient way of estimating the relative coverage on different pre-treated surfaces. Table 2 shows the fractional coverage of octadecanethiol on gold, copper and silver surfaces for different surface treatments. These values are obtained from the following equation:

Fractional coverage =
$$\frac{Q_B - Q_T}{Q_B} \times 100$$

where Q_T and Q_B respectively are the integrated cathodic charges of the octadecanethiol adsorbed surface and bare metal surface for each of the surface treatments.

Table 2

Fractional coverage of octadecanethiolmonolayer on gold, silver and copper surfaces for different surface pretreatments

PRE-TREATMENT*	GOLD	SILVER	COPPER
800 EMERY (17μm)	97.4 %	94.4 %	95.8 %
1000 EMERY (13µm)	97.4 %	90.3 %	82.2 %
1500 EMERY (9μm)	92.9 %	63.9 %	75.6 %
ALUMINA (0.05µm)	78.5 %	41.3 %	57 %
CHEMICAL ETCH	99.95 %	98.51 %	94.37 %
ELECTROPOLISHING	99.71 %		74.86 %
OXIDE FORMATION	95.40 %	79.05 %	86.05 %
EVAPORATED	95.76 %		

4.4 Study of barrier properties at different pretreated surfaces:

4.4.1 Mechanically polished surfaces:

In order to compare the different mechanically treated surfaces we have plotted the cyclic voltammograms of surfaces treated with 800 grit emery (17 μ m), 1000 grit emery (13 μ m), 1.500 grit emery (9 μ m), and alumina (0.05 μ m) polished surface after adsorption with octadecanethiol. Figures 4 (a-e), 5 (a-e) and 6 (a-e) show CV's of the blank and 17 μ m, 13 μ m, 9 μ m and 0.05 μ m particle treated surfaces respectively after thiol adsorption for gold, silver and copper respectively. It can

Legend for figures:

Potentials are referred with respect to Hg/Hg_2SO_4 (sat Na_2SO_4) reference electrode.

Figure 4: Cyclic voltammograms of Gold in 0.1 M NaOH

- a) Bare Electrode (without dipping in octadecanethiol).
- b) After treating with 800 grade emery and 30 minutes dip in 1mM octadecanethiol.
- c) After treating with 1000 grade emery and 30 minutes dip in 1mM octadecanethiol.
- d) After treating with 1500 grade emery and 30 minutes dip in 1mM octadecanethiol.
- e) After treating with 0.05 μ m alumina and 30 minutes dip in 1mM octadecanethiol.

Figure 5: Cyclic voltammograms of Silver in 0.1 M NaOH

- a) Bare Electrode (without dipping in octadecanethiol).
- b) After treating with 800 grade emery and 30 minutes dip in 1mM octadecanethiol.
- c) After treating with 1000 grade emery and 30 minutes dip in 1mM octadecanethiol.
- d) After treating with 1500 grade emery and 30 minutes dip in 1mM octadecanethiol.
- e) After treating with 0.05 µm alumina and 30 minutes dip in 1mM octadecanethiol.

Figure 6: Cyclic voltammograms of Copper in 0.1 M NaOH

- a) Bare Electrode (without dipping in octadecanethiol).
- b) After treating with 800 grade emery and 30 minutes dip in 1mM octadecanethiol.
- c) After treating with 1000 grade emery and 30 minutes dip in 1mM octadecanethiol.
- d) After treating with 1500 grade emery and 30 minutes dip in 1mM octadecanethiol.
- e) After treating with 0.05 μ m alumina and 30 minutes dip in 1mM octadecanethiol.



Figure 4



Figure 5



Figure 6

be clearly seen from Table 1 and the CV's that the integrated charge measured on the octadecanethiol adsorbed substrate increases quite significantly with the decreasing particle size of the abrasive used for polishing. This shows that a surface roughened with 17 μ m blocks the charge transfer reaction more effectively than a surface treated with a 0.05 μ m alumina particles. In fact in the case of gold, for the surfaces treated with 17 μ m and 13 μ m particles the CV's are just straight lines and the charges are hardly measurable at a slower scan rate of 20 mV sec⁻¹. Hence we have used a higher scan rate of 100mV sec⁻¹ in this case. From Table 2 it is clear that the fractional coverage decreases in a gradual manner with the decreasing particle size of the abrasive used. This change is most pronounced in the case of alumina polished surface. In other words, the surface polished with alumina is least effective as a barrier for faradic reaction compared with the one with 800grit emery. This clearly establishes a direct correspondence between the efficiency of the barrier film and the surface roughness.

Our observation of increase in coverage with increasing roughness is rather surprising and has an important bearing on the SAM formation on mechanically treated surfaces. Therefore we first studied how the real surface area changes with polishing.

Measurement of real surface area by oxygen adsorption from solution:

This method is applicable to metals showing well developed regions for oxide monolayer formation and reduction. This method can be applied to gold. Oxygen is assumed to be chemisorbed in a monoatomic layer prior to oxygen evolution with a one to one correspondence with the surface metal atoms. This implies that the charge associated with the formation or reduction of the layer is,

$$Q_0 = 2 e N_A \Gamma_0 A$$

where,

 N_A is Avogadro's number

 Γ_0 is the surface concentration of atomic oxygen ,assumed to be equal to N_M the surface density of metal atoms.

From the value of N_M per unit area the value of Q,, the reference charge density can be calculated. For polycrystalline gold this value is 400 $\mu C cm^{-2}$.

The roughness factor is calculated by dividing the charge obtained for monolayer formation for gold electrode per unit area by $400 \,\mu C \, cm^{-2}$.

Roughness factor = *Real area* / *Geometric area*

We find from these measurements that the real surface area increases, but not considerably with increasing roughness of the emery used for polishing. The roughness factor for surfaces treated with 0.05 μ m alumina, 1500, 1000 and 800 grit emery are 1.775, 2.035, 2.137 and 2.204 respectively. This shows that the increase in the real surface area from the smoothest (0.05 pm) polishing material to the coarsest (17 μ m particle emery) is only to the extent of 25%. However from Table 2, it can be seen that the surface treated with coarse particle of 17 μ m has a defect region of about 2.6% of the total area compared to 21.5% in the case of the surface polished with 0.05 μ m alumina particle. For all the three metals studied, the surfaces treated with 800 grit emery exhibits a barrier capability of an order of magnitude higher than that of alumina treated surfaces. This large increase in the barrier capability is thus not commensurate with the increase in measured roughness factor from 1.775 to 2.204 between alumina and 800 grit emery treated surfaces. An explanation for this order of magnitude increase in the defect regions is obtained from Scanning tunneling microscopic studies on the surface of gold.

In the case of chemically etched gold surface we find that the charge obtained for monolayer formation per unit area is less than $400 \,\mu C \, cm^{-2}$. The charge required for monolayer formation for certain crystallographic planes is less than $400 \,\mu C \, cm^{-2}$. This indicates that chemical etching leads to preferential

dissolution and formation of certain crystal facets of preferred crystallographic orientation.

Figures 7 (a-c) show optical microscopic photographs of polycrystalline gold specimen polished with $0.05\mu m$ alumina powder, 9 μm particle emery and 17 μ m particle emery respectively. From the photographs it is clear that the macroscopic roughness increases gradually with the particle size of the polishing material. This is of course to be expected. Scanning tunneling microscopy probes the surface at the nanometer scale and this provides a powerful tool for imaging the surface topography at this level. Figure 8 (a -b) shows the 3-D plot of 200nm x 200nm STM images of gold surface after polishing with 0.05 µm alumina and 17 µm particle emery respectively. The alumina polished surface which appears smooth and bright visually through the optical microscope can be seen to be granular with several nanometer level corrugations. Each such region is approximately 30nm in height and 60-80nm in diameter. The surface treated with 17µm particle emery is surprisingly smooth on the same scale without similar regions of roughness and steps of comparable size in contrast to its macroscopic roughness. Figures 9(a-d) show the plot of 200nm x 200nm STM images of gold surface after polishing with 0.05 µm alumina and 17 µm particle emery and the corresponding Abbot curves, where the surface heights are plotted as a function of percentage of total true area.

Abbott and Firestone [31] suggested the use of an index of the wear resistance of a surface. The curve called as the Abbott curve or the bearing area curve may be developed from a stylus trace of the surface texture and represents the length of the material intercepts as a percentage of the true length 1 and as a function of the depth irregularities. Reason developed an experimental unit for generating bearing curves having the depth expressed in terms of R_a value above and below the mean line. R_a is defined as "The arithmetical average value of the departure of the whole of the profile, both above and below its centerline,



STM images of gold surfaces treated with (a) 50 nm alumina a (b) 800 grade (17 um particle) emery (3D surface plots)

FIGURE - 8 (a-b)





STM images of gold surfaces treated with (a) 50 nm alumina and (b) 800 grade (17 um particle) emery and the corresponding Abbott curves imaged at 200 nm x 200 nm

FIGURE - 9

throughout the prescribed nieter cut off, in a plane substantially normal to the surface".

$$R_a = \frac{1}{l} \int_{0}^{l} |y| dx$$

The advantages of the plot are that it enables comparisons to be made since all curves are plotted on the same scale. Also the indeterminate characteristic of maximum peak and valley points is unimportant.

These curves show the roughness distribution on the surface of alumina polished and $17\mu m$ particle treated surfaces respectively. It can be seen the surface polished with emery has surface roughness of maximum height extending to about 16nm while an alumina treated surface has a much higher degree of roughness extending to about 60nm on the same scale.

Figures 10 (a-d) shows the $1\mu m \times 1\mu m$ STM images and Abbot curves of gold surface after polishing with 0.05 μm alumina and 17 μm particle emery respectively. It can be observed that at the larger scan range ($1\mu m \times 1\mu m$) the surface polished with 17 μm particle emery has surface roughness of maximum height extending to about 300nm while the alumina treated surface has a much lower degree of roughness extending to about 120nm on the same scale. This clearly indicates that the comparative roughness of the two surfaces depends on the length scale of measurement. At larger scales the 17 μm particle treated surface surface scales the situation is reversed.

From the above results we infer that the defects are predominantly formed on the surface corrugation regions. These regions, which are present in large numbers on the alumina polished surface allow the redox species (hydroxyl ions in this case) to reach the electrode. As the particle size of the emery used for polishing increases, the surface appears smoother at the nanometer level and rougher at a much larger scale. The larger sized particles create wider grooves on



STM images of gold surfaces treated with (a) 50 nm alumina and (b) 800 grade (17 um particle) emery and the corresponding Abbott curves imaged at 1000 nm x 1000 nm

FIGURE - 10

the surface while polishing even while removing the hills and valleys on the surface at a smaller scale. Consequently this results in a lesser number of defect sites on such a surface which is reflected in lower charge values and hence better coverage. The behaviour exhibited by the octadecanethiol covered electrodes is remarkably similar in the case of all the three metals studied in this work.

We have studied the evaporated gold surface [Au (111)] by imaging with STM. Figures 11 (a-d) show the STM images of evaporated gold at the (200nm x 200nm) and (1 μ m x 1 μ m) scan ranges and the corresponding Abbot curves. We find that the maximum surface roughness at (200nm x 200nm) range is 25nm. This value is larger than that of 17 μ m particle emery treated surface but smaller than 0.05 μ m alumina treated surface. Thus a polycrystalline surface which is treated with 17 μ m particle emery has better barrier properties compared to Au(111) single crystal surface. In the (1 μ m×1 μ m) range the maximum surface roughness is found to be around 60 nm. Figures 12 (a-b) show the 3-D STM images of evaporated gold on mica at (200nm × 200nm) and (1 μ m×1 μ m) scan ranges. We have also obtained STM images of the evaporated gold surface after adsorption with octadecanethiol. Figure 13 shows the STM images of octadecanethiol adsorbed on evaporated gold imaged at different scan ranges at different scan ranges.

4.4.2 Chemical etching, Electropolishing and oxide formation:

These surfaces show properties that are different from the surfaces which are mechanically treated that was discussed in the earlier section. In fact we find that chemical etching of gold with aqua regia and of silver and copper in nitric acid form surfaces in which the monolayer has the best blocking ability. This can be seen from the CV's in fig. 1 (b), 2(b), 3(b) and the charge - coverage values presented in Table 1 and 2. Figure 14 (a-b) shows the 200nm × 200nm STM



200 nm



60

XO

100

Evaporated gold surface imaged at (a) 200 nm x 200 nm and (b) 1000 nm x 1000 nm scan ranges and the corresponding Abbott curves





200 nm





Evaporated gold on mica imaged at (a) 200 nm x 200 nm and (b) 1000 nm x 1000 nm scan range (3D surface plots)

FIGURE - 12

a



STM images of octadecanethiol adsorbed gold on mica imaged at different scan ranges on the same location showing the formation of domains.

FIGURE - 13



1000 nm

Gold surface treated with aqua regia and imaged at different locations and the corresponding Abbott curve

FIGURE - 14

images of gold surface at different regions after chemical etching in concentrated aqua regia solution. The Abbot curve of the surface at different regions are shown in fig 14 (d-e). It is found that at this scan range of (200nm x 200nm) the maximum height of surface roughness varies at different locations with some regions being extremely smooth and certain regions being very rough. In fact the maximum roughness varies as much as 20nm to 60nm. Similar behaviour is also exhibited at larger scan sizes of $1\mu m \times 1\mu m$ where the region with the maximum height of surface roughness is around 160nm is shown in the fig 14 (c) and corresponding Abbot curve in fig 14 (f). Figures 15 (a-c) show plots of 3-D STM images of chemically etched gold surface at (200nm \times 200nm) range at two different regions on the surface and at $(1\mu m \times 1\mu m)$ range. This sort of behaviour is only to be expected for the chemically etched surface where there is no way of controlling the metal dissolution. Normally for such a surface, if we use the similar argument as for the mechanically treated surface, we would expect barrier property which is poor compared to a surface which is mechanically treated. On the contrary we find that the chemically treated surface exhibits the best barrier property among all the surfaces. We feel that the reason for this behavior lies in the fact that a chemically treated surface exposes a fresh pristine surface free from any surface contaminations and the monolayer formed on such a surface exhibits excellent blocking ability. In other words, the cleanliness of the surface far outweighs the requirement for a microscopically smooth surface.

The surface obtained obtained by electropolishing is found to be smoother than all the other surface pretreatments in the lower scan range (200nm × 200nm). Fig. 16(a-d) shows the STM images and Abbot curves of electropolished gold surface at (200nm x 200nm) and at (1 μ m x 1 μ m) range. We find that the surface roughness of maximum height to be only 6nm at the (200nm x 200nm) while it has a value of 120 at the (1 μ m x 1 μ m) range. Figure 17 (a-b) show the 3-D STM plots of electropolished gold imaged at (200nm x 200nm) and at (1 μ m × 1 μ m)





1000 nm

Electropolished gold surface imaged at (a) 200 nm x 200 nm and (b) 1000 nm x 1000 nm scan ranges and the corresponding Abbott curves.

FIGURE - 16



1000 nm

Electropolished gold surface imaged at (a) 200 x 200 nm and (b) 1000 nm x 1000 nm scan ranges 3D surface plots



range. This smoothness helps the electropolished surface to form a monolayer with effective barrier (Table 1 & 2). It is interesting to note that the charge measured on the alkanethiol adsorbed electropolished surface is considerably lower than the alumina polished surface. An electropolished surface is inevitably covered with a layer of oxide. This indicates that monolayer formation happens even on an oxidised substrate. Ron et al. [32-33] have reported that octadecanethiol adsorbs quite effectively on plasma pre oxidised gold surface. Yan et.al. [34] studied the self assembled alkanethiolate monolayers on oxidised gold formation of substrates by X-ray photoelectron spectroscopy (XPS), contact angle measurements and Near edge X-ray absorption fine structure spectroscopy (NEXAFS). They oxidised gold by exposure to atomic oxygen in vacuum. XPS revealed that gold oxide is encapsulated under the self assembled monolayer. The electropolished surface could also form the monolayer trapping the oxide underneath it.

The value of average surface roughness of maximum height at different scan ranges for different pretreated surfaces is shown in Table 3.

Surface roughness of maximum height at different scan range				
PRETREATMENT	(200nm×200nm)	(Iµm x 1pm)		
800 EMERY (17µm)	16	300		

Table 3

 ALUMINA (0.05μm)
 60
 120

 CHEMICAL ETCH
 20-60
 160

 ELECTROPOLISHING
 6
 120

 EVAPORATED
 25
 60

We wanted to find out whether an oxide covered surface could also form a self assembled monolayer. Hence we electrochemically formed oxide by holding the metal at the oxidation potential, removing it from the solution at that potential and dipping it into 1 mM octadecanethiol solution. From the cyclic voltammograms and Tables 1&2 we find that the fractional coverage is significantly high even though a thick oxide layer is present above the metal surface. The oxide which is covered with octadecanethiol monolayer is electrochemically inactive due to the barrier film formed by the alkanethiol. This incidentally also explains that inspite of being spontaneously covered with an oxide film on exposure to air, monolayer formation occurs on metals like copper and silver. In the following section, we discuss the effect of surface roughness on the barrier properties of alkanethiols using electrochemical impedance studies.

4.5 Study of effect of surface roughness on barrier properties using electrochemical impedance spectroscopy:

In order to study the effect of surface roughness on barrier efficiency we have carried out impedance studies of silver subjected to different pretreatments and adsorbed with octadecanethiol. The impedance analysis was done at a potential of 0.00 V with respect to $Hg1Hg_2SO_4(sat Na_2SO_4)$ electrode. The electrolyte was 0.1 N NaOH. At this potential silver forms silver oxide (Silver oxide is not formed at rest potential). Figure 18 shows the impedance diagram (Bode plot and Cole-Cole plot) of bare silver (0.05 µm alumina treatment) held at 0.00V in 0.1 N NaOH. Figures 19 (a-c) show the impedance plots of silver pretreated with 0.05 µm alumina powder, 17 µm emery and chemical etching which are adsorbed with octadecanethiol, held at 0.00 V in 0.1 N NaOH solution.

At 0.00 V there is an electrochemical oxidation of silver to silver oxide. Adsorption of octadecanethiol will inhibit this reaction. Thus the charge transfer resistance R_{ct} of the system will increase compared to the blank value. If the barrier efficiency of the monolayer depends on the surface pretreatment, then the



Cole-Cole plot: Silver in 0.1N NaOH at 0.00V (oxidation potential)













variation in R_{ct} should indicate the corresponding change in the barrier efficiency. We are interested in finding out the effect of surface pretreatment on this process. Table 4 shows the values of charge transfer resistance R_{ct} for different surface treatments calculated from the impedance plots.

Table 4

 R_{ct} values for different surface pretreatments

PRE TREATMENT	$R_{ct} \Omega cm^2$)
BLANK	9270
800 EMERY (17µm)	20156
ALUMINA (0.05µm)	16831
CHEMICAL ETCH	33814

We observe that the order of decrease of R_{ct} is,

Chemical etch > 17 μ m > 0.05 μ m

Thus a chemically etched silver surface shows the best barrier property compared to other surface treatments. The surface treated with $17\mu m$ emery shows better barrier properties than that treated with 0.05 μm alumina particles. This observation agrees with our earlier discussion where cyclic voltammograms show similar behaviour.

4.5.1 Effect of surface oxide:

As was described earlier an oxide covered surface can also act as a substrate for monolayer formation by alkanethiol. We have studied the effect of silver oxide in the formation of self assembled monolayer by impedance spectroscopy.

The silver electrode (0.05µm alumina treated) was held at a potential of 400 mV with respect to Hg/Hg_2SO_4 (sat Na_2SO_4) electrode for one minute in 0.1

N NaOH solution. At this potential the silver surface gets oxidised to silver oxide. The silver electrode was allowed to come back to its rest potential. Impedance spectroscopy was carried out at rest potential (-0.212 V). Figure 20 (a) shows the impedance plot of silver covered with a layer of silver oxide at rest potential.

In order to study the effect of silver oxide on monolayer formation by octadecanethiol the following procedure was adopted. The silver electrode is held at +400 mV with respect to Hg/Hg_2SO_4 (sat Na_2SO_4) reference electrode for one minute. This ensures the formation of silver oxide on the surface. The electrode is then cleaned with millipore water and immersed in a solution of 1mM Octadecanethiol for 30 minutes. Impedance analysis is carried out at rest potential (-0.212 V). The impedance plot is shown in figure 20 (b).

The double layer capacitance C_{dl} of silver-silver oxide in 0.1N NaOH is found to be 13.47 $\mu F cm^{-2}$ from figure 20(a). This value reduces to 3.36 $\mu F cm^{-2}$ after adsorption of octadecanethiol. The reduction in the value of the double layer capacitance C_{dl} clearly indicates the formation of octadecanethiol monolayer onto silver oxide. This clearly proves that the monolayer formation can occur also on oxide covered silver surfaces.

4.6 Conclusions:

Froni cyclic voltammetry, impedance and scanning tunneling microscopy studies we find that the barrier properties of alkanethiol monolayers on metal surfaces strongly depend on the surface pre-treatment of the metal surface. We find that the effectiveness of the monolayer film decreases gradually as the particle size of the polishing material is made smaller. At the outset this is rather surprising because a smaller sized particle is expected to produce a smoother surface which should help in the formation of an effective nionolayer. However we find from scanning tunneling niicroscopic studies that an alumina polished surface which appears smooth when seen through an optical microscope is actually rough at a much



Cole - Cole plot: Silver oxidised with silver oxide at rest potential





Cole-Cole plot: Silver covered with silver oxide + ODT at rest potential



lower scale and contains a large number of corrugations that aid in the formation of numerous defect sites. A mechanically formed macroscopic rough surface like the one polished with 17 μ m particle emery is actually smooth at the nanometer level with lesser number of corrugations which explains the better efficiency of the barrier film formed by the alkanethiol.

We find that microscopic surface roughness is directly related to the permeability of the monolayer. As the microscopic roughness of the surface increases there is a corresponding increase in the permeability of the monolayer. The barrier efficiency which reflects the quality of a monolayer by its ability to inhibit the electron transfer between the underlying gold electrode and a redox active molecule present in the contacting solution consequently is found to decrease. We also observe that charge obtained from the cyclic voltammograms increase if the electrodes are subject to repeated scans in all the cases. This is in agreement with the earlier results where it is reported that the repeated scans of the cyclic voltammograms into the oxide formation region increases the pinhole area incrementally rather than catastrophically [24]. The defects in the monolayer will manifest as an increase in current due to the increased accessibility of the ions in solution to the metal surface. Macroscopic roughness is not found to be as important as microscopic roughness in determining the quality of the monolayer.

Impedance studies of silver held at oxidation potential as a function of surface treatment also confirm that the effectiveness of the monolayer film decreases as the particle size of the polishing material is made smaller as borne out by R,., values.

The chemically etched surface is an exception. In this case even though the microscopic roughness is greater than that of other surface treatments, it forms a monolayer having the best barrier efficiency. We believe that this may be due to the combined effect of creation of a fresh surface during the etching process and removal of adsorbed impurities which helps in formation of such a monolayer.

We also find that an electropolished surface is extremely smooth at the nanometer scale.

Our results clearly establish for the first time, that there exists a direct correlation between the surface roughness and barrier efficiency. We also find that alkanethiols can form an effective monolayer even on oxidised metal substrates. We believe that these results and methodology adopted in this work will contribute to a better understanding of the role of surface roughness and pretreatment on the barrier properties of self assembled monolayers.

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