

CHAPTER 1

Introduction :

Surfaces, interfaces and interfacial phenomena are of great interest to people of diversified fields like chemistry, physics, biology and material science. Adsorption of different organic molecules on certain surfaces to form two-dimensional systems of molecular dimensions are of great importance to the present scientific community from the point of view of its potential application in the field of catalysts, sensors, electro-optics, molecular electronics and other nanosized materials.

The concept of thin monomolecular films is nearly two centuries old. The first scientific studies of oil films on water was performed by American scientist Benjamin Franklin [1]. Later, Pockels invented a new method of determination of thickness of thin films of molecular dimension. Her work was published in the journal *Nature* [2] in 1891 under the request of Lord Rayleigh. In the year 1920, Langmuir published his famous work on the study of two dimensional molecular films at the liquid-gas interface [3] (the Langmuir Film). In the year 1934, Blodgett transferred the floating film on liquid surfaces to solid surfaces [4,5] (Langmuir –Blodgett or L-B films).

The Langmuir-Blodgett method consists of transferring to a substrate by contacting the substrate with a compressed organized layer at the air-water interface [6-8]. The head group is hydrophilic and the tail group is hydrophobic. The orientation of the transferred monolayers depends on the wetting properties of the substrate. Multilayers can also be formed by

successive dipping of the substrate into the air-water interface. These films have application in the field of sensors, photoresists, non-linear optics.

In addition to L-B method, molecular self-assembly is another method of forming a monolayer. The Self-Assembled monolayer is the spontaneous adsorption process of organic molecules on some substrates to yield structurally well defined monolayers [8-10]. One type of organized monolayers can be formed on noble metal surfaces like gold, silver and copper by the self-assembly of alkanethiol molecules. Such organized SAMs of alkanethiol molecules exhibit several interesting properties and have several potential applications like corrosion inhibitions, lubrications, wetting, sensors, molecular electronics etc.

This thesis deals with the adsorption behaviour of organic thiol monolayers on gold. More specifically, we focus on the effect of different solvents on the structure, integrity and interfacial properties of SAMs of alkanethiol and other thiol derivatives like aromatic thiol, dithiol, hydroxythiol, carboxylic acid thiol, amino thiol, thiocholesterol etc. We have carried out such studies using electrochemical techniques like cyclic voltammetry, electrochemical impedance spectroscopy and non-electrochemical techniques like Grazing Angle FT-IR Spectroscopy and Scanning Tunneling Microscopy (STM). We have also adsorbed alkanethiol molecules to form monolayers on gold microelectrodes of diameter 40 and 12.5 μm fabricated in our laboratory and studied the effect of solvents on such monolayers.

This chapter is divided into three parts. In the first part, the formation and characterization of alkanethiol SAMs on gold is discussed in details. We also briefly review different methods of characterization of alkanethiol SAMs. The second part deals with the general introduction to the field of

microelectrodes and its utility on electrochemical studies. In the third part, we have discussed the aim and scope of our studies.

1.0 Introduction to Self-Assembled Monolayers (SAMs) :

The phenomenon of self-assembly has been known for the last 50 years, but not until recently people took interest to this versatile field. Self-Assembled Monolayers are ultrathin organic films of few nanometers thickness, which are formed spontaneously by immersion of appropriate substrate into dilute solution containing organic molecules. There are several methods of self-assembly that yield organic monolayers. These include organosilicon on hydroxylated surfaces [11-13], alkanethiols on gold [14,15], silver [16] and copper [17], dialkyl sulphide on gold [18], alcohols and amines on platinum [19] and carboxylic acids on aluminium oxides [20] and silver [21].

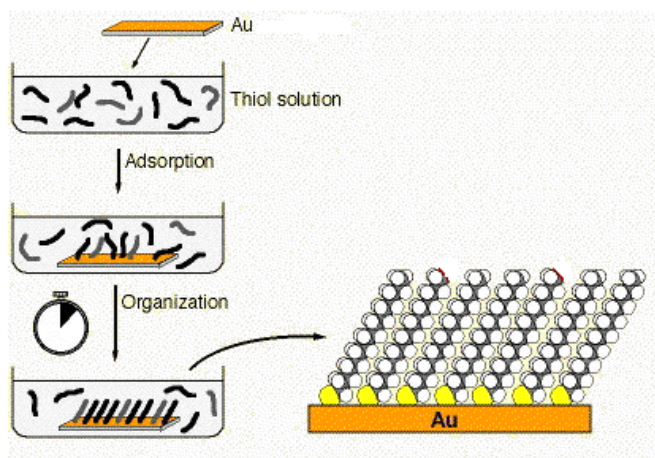
From the energetics point of view, self-assembly can be divided into three steps. The first step is the chemisorption of the head group onto the substrate. The bonding can be covalent in the case of alkyltrichlorosilanes on hydroxylated surfaces, covalent but slightly polar for alkanethiol monolayers on gold, ionic bond for carboxylic acids on AgO/Ag. The energies associated with such chemisorption are of the order of tens of kcal/mol (in case of thiolate on gold it is 40-50 kcal/mol). The second step is the inter chain van der Waals interactions among the alkyl group, where the energy associated with it is only few kcal/mol. The third and the final step is the reorientation of the terminal groups. In the case of simple alkanethiol, methyl is the terminal group. These surface groups are thermally disordered at room temperature, which are evident from the FTIR studies on

monolayers [22]. The energies associated with this process are of the order of few kT s, where k is Boltzmann constant and T is absolute temperature.

In 1983, Nuzzo and Allara [18] published the first paper deal with the formation of organized dialkyl sulphide monolayers on gold.

1.1 Monolayer formation :

The process of formation of SAMs of alkanethiol on gold is very simple. A clean, fresh gold substrate is immersed into a dilute solution of alkanethiol molecules in an organic solvent. The time of immersion varies from few minutes to several hours. The concentration of the thiol molecules and the immersion time of the substrate in the adsorption solvents play very important role in the self-assembly process. Typically, the concentration of the thiol is at millimolar levels, although concentration from micromolar to neat liquid thiols have been reported. Ethanol has been the most common solvent for the formation of alkanethiol monolayers on gold, although several other solvents like THF, acetonitrile, hexane have been used by some people. It is also possible to form monolayer by gas-phase deposition. An early work of self -assembly in the gas phase was reported by Crooks et al.



Self assembly of alkanethiol on gold

[23]. In addition to simple alkanethiol SAMs, monolayers with different terminal functional groups, aromatic thiols, thiol with attached polymers, lipids, proteins, peptides and redox centers have been studied.

Since the discovery of SAMs of alkanethiol, a lot of efforts have been taken to obtain the most blocking and highly oriented monolayers on gold by varying different parameters of self-assembly process like substrate morphology, substrate cleanliness, substrate pre-treatment, alkanethiol concentration, adsorption time, adsorption solvent, alkanethiol purity etc.

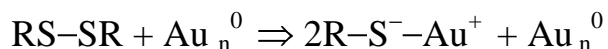
Morphology of the substrate means the degree of crystallinity of the substrate. The substrate may be polycrystalline or single crystal. Most of the work of SAMs of alkanethiol has been done on evaporated or sputtered gold substrate deposited on freshly cleaved mica, polished single crystal silicon or glass under special conditions. The gold substrates exhibit predominantly Au(111) character [24-26]. Although, a single crystalline substrate containing a well defined crystal face is important for many surface analytical methods like electron diffraction, scanning tunneling microscopy, there is no clear and consistent proof that a single crystalline substrate is essential for the formation of pin hole free SAMs.

Substrate cleanliness is essential before the formation of SAMs. The usual cleaning methods include strong heating of the substrate, exposure of the substrate to argon, oxygen plasma, ozone or UV radiation, immersion of the substrate in strong oxidizing agents, electrochemical potential cycling in dilute acid solution.

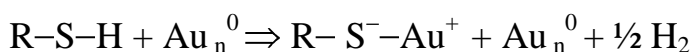
“*Piranha*” solution, which is a mixture of concentrated sulphuric acid and 30% hydrogen peroxide in 3:1 ratio is a common oxidizing agent to clean the Au substrate before monolayer formation.

1.2 Nature of bonding :

The nature of bonding between the alkanethiol molecules and Au substrate is still a matter of considerable research. Both alkanethiols and disulphides adsorbed on gold to form the same gold thiolate (RS^-) species [25,27]. The reaction of dialkyldisulphides with gold is an oxidative addition,



In the alkanethiol case, the reaction may be considered as an oxidative addition of the S-H bond to the gold surface, followed by a reductive elimination of the hydrogen. When a clean gold surface is used, the proton probably ends as H_2 molecule.



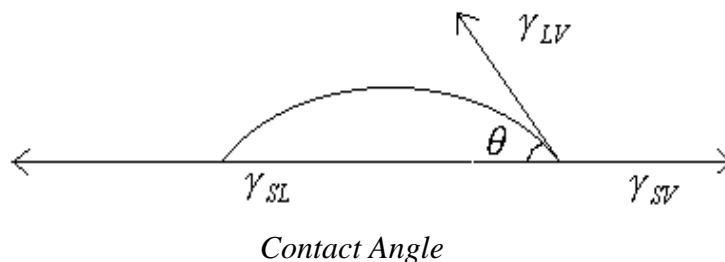
The combination of hydrogen atoms at the gold surface to give H_2 molecule may be an important exothermic step in the overall chemisorption energies. During the chemisorption, formation of thiolate have been verified by XPS [15, 28-29], FTIR spectroscopy [30], FT-mass spectrometry [31], electrochemistry [32] and Raman spectroscopy [25]. The bonding of the thiolate group to the gold surface is very strong (bond strength is approximately 40 kcal/mol).

1.3 Methods of characterization of SAM :

Several techniques have been used to characterize the SAMs of alkanethiol and from the characterization, a lot of information like monolayer structure, molecular conformation, orientation, pinhole defect density have been obtained.

1.3.1 Contact angle measurement :

The phenomenon of wetting or non-wetting of a solid by a liquid is better understood by studying what is known as contact angle. One of the important properties of monolayer is the wetting behaviour [14, 33-34].

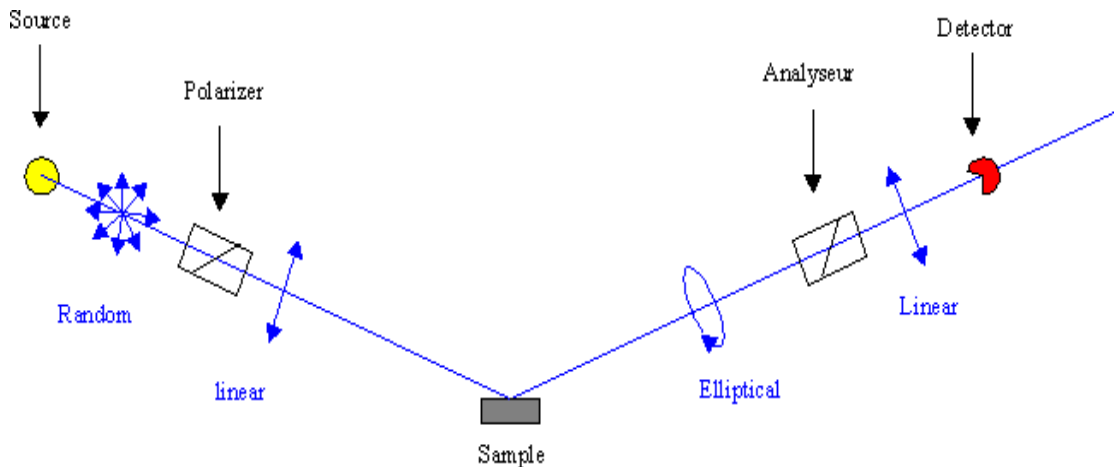


The contact angle is measured by placing a small drop of a liquid on a horizontal solid substrate. The drop of liquid forming an angle may be considered as resting in equilibrium by balancing the forces involved; namely the interfacial tension between solid and liquid SL , between solid and vapour SV and between vapour and liquid LV . The angle within the liquid is known as contact angle or wetting angle. Both the advancing angle (drop volume increasing) and the receding angle (drop volume decreasing) are of interest, since the hysteresis in the contact angle is an indicative of degree of order in the monolayer. For homogeneous monolayers, close packing and high degree of orientation generate a surface in which effectively only the terminal group of the tail is exposed outside. These types of surfaces exhibit strongly characteristic wetting properties. The highest values of contact angles with water are observed in case of alkanthiol monolayers with terminal CH_3 or CF_3 groups. These high wetting contact angles are part of the evidence that the monolayer chains are well oriented so that only the terminal group is exposed to the contacting liquid. On the other hand monolayers containing very polar terminal groups like OH or $COOH$

exhibit almost zero contact angle (complete wetting). Whitesides and his co-workers have extensively used contact angle method to explore the structure of SAM [35-37]. The kinetics of thiol adsorption can be followed by contact angle [14].

1.3.2 Ellipsometry :

The name “ellipsometry” stems from the fact that the most general state of polarization of light is elliptic. The technique has been known for almost a century, and at present it has many standard applications. The determination of monolayer thickness is the first characterization method of monolayer. At present, ellipsometry is the most common optical technique to determine the thickness and refractive index of thin homogenous films [38]. In



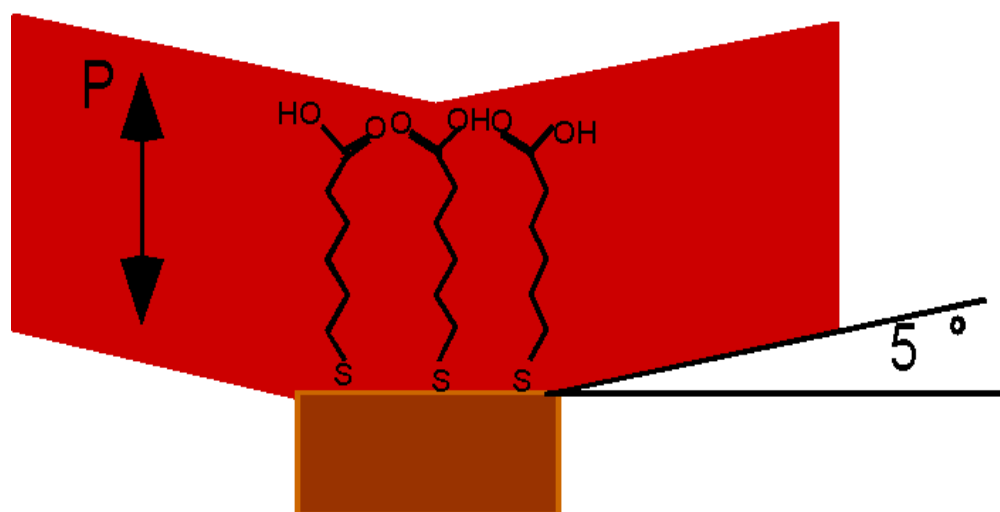
Schematic diagram of ellipsometer

ellipsometry, a well defined polarization state of light is reflected from the substrate and changes in the polarization state is measured. The changes are well defined by two parameters Ψ & Δ . The parameter Ψ is defined as the change in the ratio of intensities for the inplane and out of plane component of polarization, whereas Δ is related to the phase difference between the in plane and out of plane component of the reflected light. By first measuring the values of the parameters Ψ & Δ for bare substrate and then repeating for

monolayer coated substrate, the monolayer thickness can be determined. With the help of ellipsometry, it had been proved that a single molecular layer is formed during the self-assembly of alkanethiol molecules [39,40]. For SAMs composed of alkanethiol molecules, the ellipsometric thickness increases linearly with the number of methylene units in the chain for $n > 5$, where n is the number of methylene units in the chain.

1.3.3 Infrared and Raman spectroscopy :

Infrared (IR) spectroscopy is a powerful tool for the study of molecular packing and orientation in ultrathin organic films [15,41]. The spectrum is obtained using either internal or external reflection modes. The internal



reflection mode is known as the (ATR) Attenuated Total Reflection Spectroscopy, whereas the external reflection mode is known as Reflection-absorption or Grazing Angle Spectroscopy. The grazing angle reflection measurements provide the greatest sensitivity for ultrathin organic films on reflective surfaces, typically metals. The reflection-absorption spectrum for a monolayer adsorbed on a metal surface is measured mostly at higher angle of incidence, and only allows the p-polarization component of incident light to pass [42]. The p-polarization component is parallel to the plane of incidence. The s-polarization component of incident light is perpendicular to

the plane of incidence. Hence the s-polarization component of incident light does not interact with ultrathin film samples on metal and therefore does not contribute to the spectral signal. This results in very high quality, clean spectra. The spectrum obtained on a ultrathin organic film coated metal substrate is ratioed with a suitable blank spectrum (taken on a bare substrate) to obtain the absorbance spectrum of the monolayer. The relative intensities of the absorption peaks in the spectrum are affected by the average orientation of transition dipoles relative to surface. A transition dipole parallel to the metal surface will exhibit a greatly attenuated peak relative to the transition dipole perpendicular to the metal surface. From these comparisons, the average orientation of the monolayer chains and the terminal groups are obtained. Peak positions also give information about the dynamic behaviour of the monolayer. A pioneering work in the area of grazing angle FTIR spectroscopy on monolayers was done by Allara and Swalen [43]. The C-H stretch region is quite characteristic for long-chain alkyl containing monolayers. The measured intensities of the CH₂ stretching mode can be used to measure the average tilt of the chain axis from the surface normal [44]. Nuzzo et al. [18,29] and Porter et al. [15] used this technique to estimate the orientation of the chain, coverage, packing density & average tilt of the monolayer in long-chain alkanethiols and disulphides on gold. Finklea et al. [45] also reported the grazing angle spectra for alkanethiol monolayers on gold. Ulman used this technique to compare the monolayers of alkanethiols on gold and silver surfaces [16]. It was found that on an Au (111) substrate alkanethiols exhibit all trans conformation with an average tilt of 30° from the surface normal. In addition to this, Allara and Nuzzo [20,44] studied the adsorption of n-alkanoic acid on aluminium oxide surface using surface IR spectroscopy.

Resonance Raman and IR spectroscopies have same set of selection rules at the surface; i.e., transition dipoles that are parallel to the surface are not detected by a p-polarized light. Surface-Enhanced Raman Scattering (SERS) was first observed for samples of pyridine adsorbed on roughened Ag surfaces [46,47]. Sandroff et al. studied SERS of organic sulphides adsorbed on silver [48]. Sandroff et al. [49] observed SERS spectrum of hexadecanethiol adsorbed on silver island films. This monolayer has all-trans conformation, but on contact with chloroform there was a decrease in the numbers of trans bonds. Thus, Raman spectroscopy serves as a tool in the understanding of self-assembly process, order-disorder transitions, and other molecular events in ultrathin organic films.

1.3.4 Surface potential :

The surface potential is an important tool for analysis of electrical structure of surfaces, i.e. the distributions of polar vs nonpolar groups. Surface potential measurement can be done both on air-water interface and on solid substrates. Evans et al. studied the surface potential as a function of alkyl chain length in alkanethiol monolayers on gold [50].

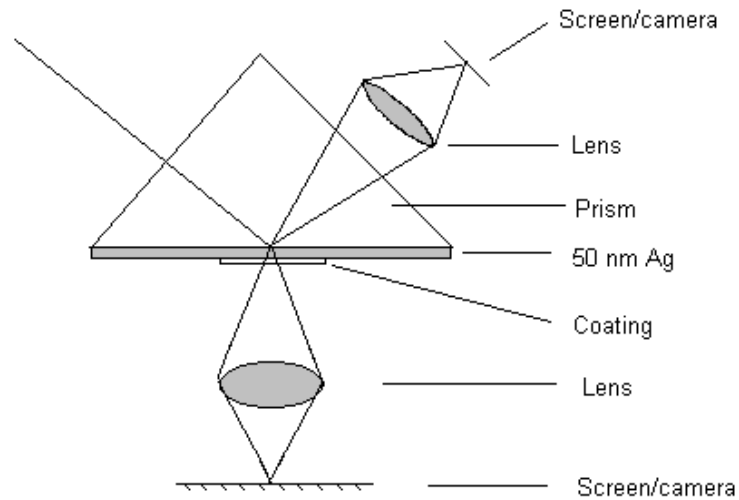
1.3.5 Quartz Crystal Microbalance :

The Quartz Crystal Microbalance (QCM) is an exciting tool for the electrochemist, who can follow both the current flow and the weight change of the electrode simultaneously [51,52]. This is a valuable tool for studying reactions which involve films, adsorbates, metal deposition, corrosion, monolayer formation. It is sensitive enough to detect a fraction of monolayer of most materials [53]. The QCM is a piezoelectric device capable of extremely sensitive mass measurement with several nanogram sensitivity. It oscillates in a mechanically resonant shear mode by application of an

alternating, high frequency electric field using electrodes which are usually deposited on both sides of the disk. The mass sensitivity arises from a dependence of the oscillation frequency on the total mass of the crystal (usually disk shaped), its electrode and contacting materials on its surface.

1.3.6 Surface plasmon spectroscopy :

Surface plasmons are most commonly created at the interface between a metal such as gold or silver and a dielectric material such as air or water. A surface plasmon consists of a resonant excitation, commonly by optical radiation, of the electrons at the surface of a metal resulting in an associated surface bound and evanescent electromagnetic wave of optical frequency. The evanescent wave has a maximum intensity at the interface and decays exponentially away from the interface. Surface plasmon spectroscopy [54] is based on the minimum in reflectance observed when monochromatic light is reflected internally from a thin metal layer between two dielectric media. The position and the shape of the reflectance minimum as a function of incident angle can be transformed into the film on a metal surface. The method is used in the detection of volatile organic compounds in gas and liquid phase with polymers, oriented liquid crystals, and bimolecular interaction on surfaces. This method has been used to monitor surface reactions of SAMs on gold surfaces in aqueous media [55,56]. Surface plasmon spectroscopy has also been used in the measurement of thickness of lipids and adsorption of proteins on SAMs.

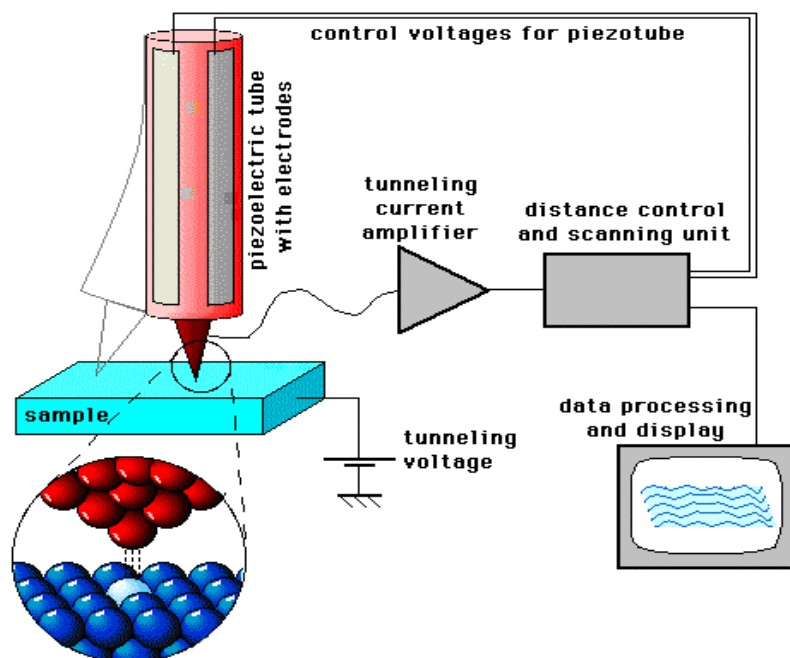


Schematic setup of surface plasmon microscopy

1.3.7 Scanning Tunneling & Atomic Force Microscopy :

Scanning Tunneling Microscopy (STM) is a new and versatile tool in the area of surface science. It was invented by Gerd Binnig and Heinrich Rohrer [57] at the IBM research institute in Zurich. STM has the advantage of studying atomically smooth conducting surfaces in a variety of environments like Ultra High Vacuum (UHV), air, electrolytic media etc. The basic principle of STM is based on the tunneling of electrons across the insulating gap (either air or vacuum) between a chemically inert, sharp metallic tip like Pt-Ir/Rh, Pt, W and a conducting material usually a metal or a semiconductor by the application of a small bias voltage, when the tip is brought very close (~ 1 nm) to the sample without any physical contact. As a result a small current (pA to nA) flows between the tip and the conducting sample [58,59]. Actually, the STM image corresponds to a contour map of local density of states of atoms on a conducting sample. The tunneling current is very much sensitive to the distance between the tip and sample.

There is a change of current of an order of magnitude for a change of gap separation by 0.1 nm. The STM can be operated either in constant current or in constant height mode. In the constant current mode of operation, the tip height above the sample is adjusted in such a way by the application of a feedback voltage that the current will remain constant, and the image is obtained as a map of this feedback voltage versus the lateral x & y coordinates. In the constant height mode, the tip is scanned over a sample in the same plane without adjusting the tip height. As a result the tunneling current will change as a change of tip-sample separation. Thus, the current is recorded as a function of lateral coordinates. The imaging of organic molecules adsorbed on conducting substrates by STM is challenging due to the low conductivity of organic films. Hallmark et al. [60] studied monolayers and multilayers of long alkyl chains containing octadecyltrichlorosilane and Cd arachidate. STM has been extensively used by different groups to study alkanethiol SAMs coated Au substrates [61,62]. While imaging SAM coated metals using STM, damage to the monolayer and substrate can be prevented by avoiding prolonged scanning at high current densities. STM reveals that the alkanethiol monolayer on Au (111) substrate forms a $(\sqrt{3}\times\sqrt{3})R30^\circ$ overlayer structure [41,61]. In contrast to STM, Atomic force Microscope (AFM) can image atoms on both conducting and non conducting surfaces [63]. In AFM, the tip of a flexible force-sensing cantilever stylus is scanned over the surface of the sample. The force acting between the cantilever and sample surface causes deflections in the cantilever, which can be detected and utilized as the feedback signal.

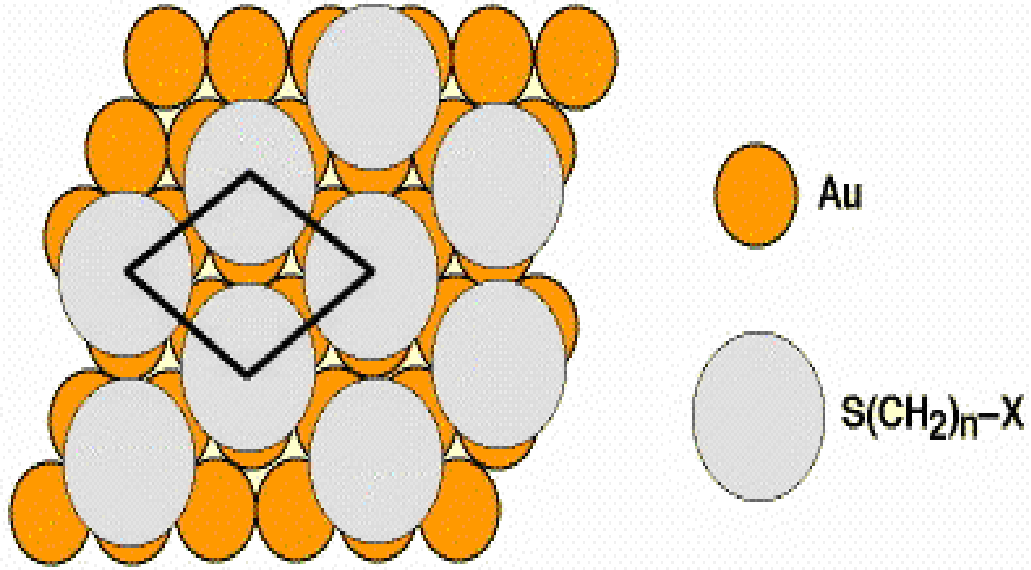


Schematic diagram of STM

1.4 Monolayer structure :

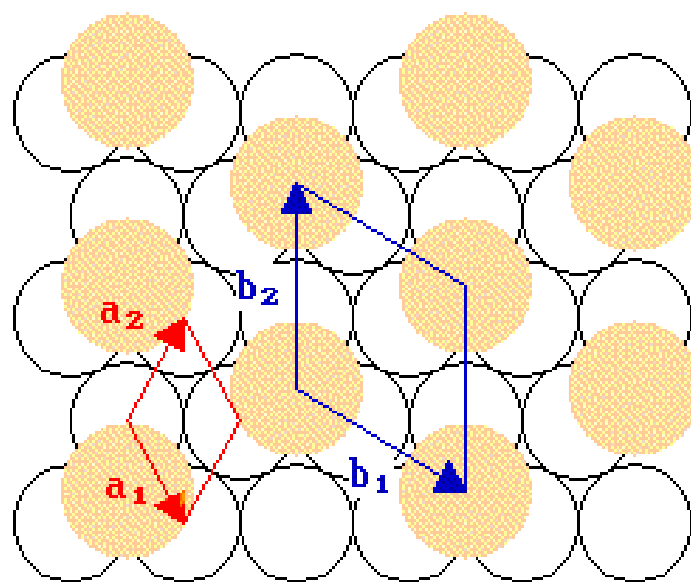
Alkanethiol molecules form highly ordered SAMs on gold substrates, which have been well characterized using a variety of surface analytical tools. Most of the work of SAMs of alkanethiol have been done on evaporated or sputtered gold substrates deposited on freshly cleaved mica, polished single crystal silicon or glass under special conditions. The gold substrates exhibit predominantly Au (111) character [24-26]. Although, a single crystalline substrate containing a well defined crystal face is important for many surface analytical methods like electron diffraction, scanning tunneling microscopy, there is no clear and consistent proof that a single crystalline substrate is essential in the formation of pin hole free SAMs. Electron diffraction and Scanning tunneling microscopy reveal that the alkanethiol monolayer on Au (111) substrate forms a $(\sqrt{3}\times\sqrt{3})R30^\circ$ overlayer structure [41,61]. The overlayer structure can be understood as follows. The vectors a_1 and a_2 define the unit cell of Au (111) substrate and b_1 & b_2 define adsorbate unit

cell. The b_1 & b_2 vectors are longer than a_1 & a_2 vectors by a factor of $\sqrt{3}$ and the angle between b_1 & a_1 vectors (between b_2 & a_2 vectors) is 30° . So the adsorbate unit cell is greater by $\sqrt{3}$ times and rotated by 30 degrees with respect to the substrate unit cell.



($\sqrt{3} \times \sqrt{3}$)R30° overlayer structure of alkanethiol SAMs on Au (111)

The spacing between the adjacent sulphur atoms in this structure (4.99 \AA) is about 3 times larger than the van der Waals diameter of sulphur atom (1.85 \AA) to minimize the sulphur-sulphur interactions. This distance is also greater than the distance of closest approach of the alkyl chains (4.24 \AA). Therefore the chains tilt by an angle 30° with respect to surface normal to maximize their van der Waals interactions [64]. Depending on the chain length and the terminal group, various superlattice structures are superimposed on the ($\sqrt{3} \times \sqrt{3}$)R30° overlayer structure. The most common superlattice is the c(4×2) reconstruction.



Unit cell of the adsorbate

1.5 Characterization of SAMs by electrochemical techniques :

For electrochemical studies, alkanethiol coated Au electrode can be used as working electrode. Cyclic voltammetry and capacitance measurements have been widely used to characterize SAMs [8]. One of the main feature of monolayers on electrodes is their ability to inhibit the access of ions and redox molecules to the electrode surface. The degree of packing of SAM on the gold electrode is obtained by comparing the dielectric constant from electrode capacitance measurements [8,15]. There are several methods of determining the surface coverage of monolayer on electrode surface. Rubinstein and Sabatini [65] have used the characteristic gold oxide stripping peak in the cyclic voltammograms of gold electrodes in sulphuric acid to measure the fractional surface coverage θ . An alkanethiol monolayer on gold has a capacitance value in the order of $1-2 \mu\text{F cm}^{-2}$ which is much smaller than bare gold electrode. This decrease in capacitance corresponds to the presence of a low dielectric constant layer between the electrode and the

electrolyte. The capacitance is determined from the cyclic voltammetry in absence of redox species. The interfacial capacitance is the combination of two capacitances in series; the monolayer capacitance C_m & the double layer capacitance C_d . When capacitance is measured at a concentrations of electrolyte above 0.1 M, the double layer capacitance is greater than $100 \mu\text{F cm}^{-2}$ and total capacitance is dominated by C_m . The simplest expression for C_m is based on Helmholtz model [15]:

$$C_m = \frac{\epsilon_m \epsilon_0}{d}$$

where d is the thickness of the double layer, ϵ_m is the static dielectric constant of the monolayer and ϵ_0 is the permittivity of free space ($8.854 \times 10^{-12} \text{ F m}^{-1}$). This expression is consistent with the nearly constant capacitance with respect to electrode potential seen in cyclic voltammetry.

The plot of the reciprocal of the interfacial capacitance versus the chain length is linear for alkanethiols containing 10 or more methylene units. From the slope of this plot, the effective dielectric constant of the monolayer is obtained. If the thickness increment is 1.3 \AA per methylene group (corresponding to all trans alkane chain with 0° tilt), then the effective dielectric constant is 2.6. On the other hand, for a thickness increment of 1.1 \AA per methylene group (corresponding to all trans alkane chain with 30° tilt), the effective dielectric constant was found to be 2.3 [15]. The typical dielectric constants for a pure aliphatic hydrocarbon & polyethylene are 2.0 and 2.3 respectively. These values are in good agreement with the experimental findings, which indicates that long chain alkanethiols have very low permeabilities for ions in aqueous medium. The interfacial capacitance of the monolayer coated electrode is affected by the change in terminal groups [41]. The ionic permeability of the monolayer is also

affected by the packing density of it. IR study of the peak positions for the CH₂ stretching modes suggests that the –COOH terminated SAM is more liquid like, while –CF₃ or –CH₃ terminated SAM is more crystalline. Hence, the former one is more permeable than the latter.

Cyclic voltammetry can probe the presence of pinholes & defects in the monolayer. A pinhole is defined as a site at which the electrode surface is accessible to the redox molecules and ions. So not only the adsorbed molecules are absent in a pinhole, but also the tails of nearby adsorbed molecules do not block at this site. A defect is defined as the site where ions and redox molecules can approach the electrode surface at a distance shorter than the thickness of the monolayer. Close packed SAMs block various kind of faradaic processes like metal oxidation, underpotential deposition of metals, oxidation and reduction of solution species etc. SAMs can passivate the oxidation of gold. It is reported in the literature [8,65] that the gold oxide stripping current in acidic or alkaline medium offers the estimation of the area fraction of the pinholes present in SAM coated gold electrode. The oxidation of gold can only occur if the water molecules or hydroxyl ions can directly access the electrode surface through the pinholes. Hence, the measured charge from the area under the oxide stripping peak is indicative of defect sites in the SAMs. The typical values of area of fraction of pinholes present in a long chain SAMs range between 0.01 and 0.0001 [8].

The second main effect of a blocking SAM is the inhibition of bulk deposition of metals at potentials close to the thermodynamic potentials and also underpotential deposition (UPD) of metals at potentials well positive of thermodynamic potentials.

The third main effect of the blocking SAMs is the inhibition of redox reactions in which both the oxidized and reduced forms of redox couples are

soluble. Various factors like heterogeneous rate constant for electron transfer, size and solvophilicity of redox species, mechanism of electron transfer (inner sphere versus outer sphere) affects the barrier properties of SAMs.

From the study of literature, we find that relatively less attention has been paid to the study of blocking properties of alkanethiol SAMs in non-aqueous solvents primarily due to their perceived instability in these solvents. With this in view, we have studied the effect of different solvents on the structure, integrity and interfacial properties of different organic thiol monolayers using different electrochemical and non electrochemical techniques.

1.6 Ultramicroelectrodes :

Electrodes with extremely small dimensions, in the order of micrometer or less are defined as ultramicroelectrodes. Initially, microelectrodes were used for biological and medical research [66]. In early eighties, Fleischmann and his coworkers at the Southampton Electrochemistry group exploited the versatile properties of microelectrodes in electrochemical studies. The ultramicroelectrodes, due to their extremely small size, have certain unique characteristics, which make them ideal for studies involving high resistive media, high speed voltammetry and *in vivo* electrochemistry in biological systems [67,68]. They exhibit very high rate of mass transfer which combined with low ohmic drop and double layer charging current make them powerful tool for studies of fast heterogeneous kinetics at very low concentrations. Due to the small electrode area, the current associated with microelectrode is very small, of the order of nA to pA and the current

densities are very high. The combinations of high current densities and low currents provide new applications in the field of analysis, sensors and Scanning Electrochemical Microscopy (SECM) [69] and studying even corrosion processes in closely defined spaces.

1.7 General features of ultramicroelectrodes :

Microelectrodes make it possible to carry out experiments which is not possible using conventional size macroelectrodes. This is due to the considerable differences in electrochemical responses between micro and macroelectrodes.

Due to the small area of microelectrodes, the double layer capacitance is reduced relative to macroelectrodes. This allows the electrode potential to be changed rapidly, which can be utilized in voltammetric measurements in submicrosecond time scale [70,71]. At normal time scales, cyclic voltammograms obtained with ultramicroelectrodes differ significantly compared to macroelectrodes. The voltammograms is sigmoidal shaped analogous to the s-shaped polarograms obtained with dropping mercury electrode or rotating disk electrodes. The rate of mass transport (diffusion) plays important role for the shape of voltammograms. At large electrodes, mass transport occurs mostly perpendicular to the electrode surface (planar diffusion). The result is a typical peak-shaped voltammogram for large area macroelectrodes. For a reversible redox process, the peak current follows Randles-Sevcik equation [72,73]. The expression is given by

$I_p = (2.69 \times 10^5) n^{3/2} C_o^* D^{1/2} v^{1/2}$, in which I_p is the peak current density ($A\ cm^{-2}$), n is the electron stoichiometry, D is the diffusion coefficient ($cm^2\ s^{-1}$) of the electroactive species, C^* is the bulk concentration of the electroactive species, v is the scan rate (Vs^{-1}). On the other hand, for a microelectrode a s-

shaped voltammogram is obtained at lower scan rates, which changes into peak shaped at very high scan rates. At lower scan rates, the rate of electrolysis is almost equal to the rate of diffusion and the diffusion takes place in a hemispherical fashion, which is a time-independent process. Hence it produces steady-state s-shaped voltammogram. At higher scan rates, the rate of electrolysis exceeds the rate of diffusion to a larger extent. At such a fast time scales, redox species take longer time to diffuse. Hence the current changes with time, and peak shaped voltammograms are obtained in those cases. The diffusion processes occurring at the ultramicroelectrodes can be understood by solving the diffusion problems for dropping mercury electrodes used in polarography. For a spherical electrode (radius r), current is given by, $i_{\text{spherical}} = nFADC^* [1/(\pi Dt)^{1/2} + 1/r]$, $A = 4\pi r^2$ is the area for a spherical electrode. According to this equation at large time scales, the current should be time independent. So for a macro electrode the current due to semi-infinite planar diffusion is given by the Cottrell equation $i_{\text{planar}} = nFADC^*/(\pi Dt)^{1/2}$. So $i_{\text{spherical}} / i_{\text{planar}} = 1 + (\pi Dt)^{1/2} / r$. The parameter $(Dt)^{1/2} / r$ will determine when the current will be predominantly steady state in nature. Saito [74] has examined the steady state nature of current at disk microelectrodes and obtained the expression $i = 4nFDCr$, where the steady state current is related to the electrode radius r . So one can determine the dimension of a microelectrode by directly measuring the steady state current from the s-shaped voltammogram, provided the value of D is known. For a redox reaction with unknown D value, the above expression can be used to determine the diffusion coefficient D . Since the steady state current is proportional to the bulk concentration of electroactive species, the above expression can also be used in determining unknown concentration of some electroactive species. Now the currents generated in a microelectrodes are

dependent on the electrode geometry. Microelectrodes of different geometries are commonly found in the literature [67,75]. Among the common geometries are disks, rings, and bands. The current associated with microelectrode is very small, of the order of nA to pA and consequently the current densities are very high compare to normal sized macroelectrodes. Current densities of upto 70 A cm^{-2} have been reported [76]. Since current density determines the ratio of Faradaic to non-Faradaic current for a cyclic voltammograms, the cyclic voltammograms obtained in case of microelectrodes are almost unaffected by background current. Since the current is very small, the corresponding iR drop for a microelectrode is negligible. Hence, microelectrodes can be used to study voltammograms in absence of supporting electrolytes and also in highly resistive media like non-aqueous solvents, polymers, gaseous interfaces, which is not possible with macroelectrodes. Due to small iR drop, microelectrodes are utilized to carry out voltammograms at very high scan rates (10^6 Vs^{-1}). The voltammograms are also free from double layer charging current. Microelectrodes also possess large mass transport coefficient m ($m=D/r$), where D is the diffusion coefficient and r is the electrode radius. Due to high rate of mass transfer, microelectrodes can be used to measure the rate constants and other kinetic parameters of very fast heterogeneous charge transfer reactions. Kinetic parameters for rapid homogeneous processes can also be determined only if the diffusion limited current is dependent on the homogeneous kinetics.

Ultramicroelectrodes are available commercially from most companies specializing in electrochemical apparatus, but the cost is very high and electrodes of variable diameters and geometries are not available. Hence, we have fabricated disk shaped gold and platinum microelectrodes

with diameters of 10-50 μm by sealing sodalime glass with metal microwires. The electrodes were characterized by performing cyclic voltammetry in aqueous and acetonitrile solution. We have also formed monolayers of alkanethiol and other organic thiol on Au microelectrodes and studied the effect of different non-aqueous solvents on the structural integrity and barrier properties of SAMs.

1.8 Aim and scope :

Since the discovery of alkanethiol SAMs on noble metal surfaces, various efforts have been taken by different groups to achieve most blocking and almost defect free monolayer. Different factors like substrate morphology, alkanethiol purity, deposition solvent, deposition time, alkanethiol concentration can be controlled to achieve this. In this thesis, we mainly discuss the effect of different solvents on the structure, integrity and interfacial properties of SAMs of alkanethiol and other thiol derivatives like aromatic thiol, dithiol, hydroxythiol, carboxylic acid thiol, amino thiol, thiocholesterol etc.

We find from literature that relatively less attention has been paid to the study of blocking properties of alkanethiol SAMs in nonaqueous solvents primarily owing to their perceived instability in these solvents. However, nonaqueous solvents provide a wide range of unique properties which can be usefully exploited for various applications involving SAMs. In addition to this the electrochemistry involved in non-aqueous solvents is novel from the point of view of solubility, chemical stability of redox probe molecules over wide potential ranges which is not possible in aqueous media to investigate the stability and structural integrity of alkanethiol SAMs. With

this in view, we have studied the electron transfer barrier properties of the monolayers formed by both neat and dilute ethanolic alkanethiols of different chain lengths (dodecanethiol and hexadecanethiol) in seven non aqueous solvents viz., propylene carbonate, acetonitrile, ethanol, formamide, acetic acid, dimethyl formamide (DMF), and dimethyl sulphoxide (DMSO) using cyclic voltammetry and electrochemical impedance spectroscopy. In this context, we have also found out the probable mechanism of ferrocene electron transfer reaction in the presence of highly insulating alkanethiol monolayer on gold in these non-aqueous solvents. The barrier properties of different alkanethiol derivatives like hydroxy and carboxylic acid thiol, aliphatic and aromatic dithiol SAMs were also carried out in different non-aqueous solvents.

We have carried out comparative studies on SAMs formed in ethanolic solution of alkanethiol as well as from neat alkanethiol. The SAMs have been characterized using electrochemical techniques like cyclic voltammetry and electrochemical impedance spectroscopy as well as by non-electrochemical techniques like Scanning Tunneling Microscopy (STM) and Grazing Angle FT-IR Spectroscopy.

There has been voluminous amount of work carried out on the alkanethiol self assembled monolayers prepared in ethanol, which due to its low toxicity, low cost, and high purity, has been a preferred solvent for the formation of alkanethiol monolayers on gold. Several other solvents such as hexane, hexadecane, chloroform and acetonitrile have been also used though much less frequently. However, from literature we find that there has not been any detailed electrochemical studies aimed at evaluating the barrier properties of the alkanethiol monolayers formed in different solvents. We have evaluated the barrier properties of alkanethiol SAMs formed in

different non-aqueous solvents using electrochemical impedance spectroscopy and also examined the effect of adsorption medium on the nature of SAM such as its permeability, hydrophobicity and other interfacial properties.

We find in literature that the time duration of dipping the gold sample in adsorbing medium often vary from a few hours to several days. It is not clear whether dipping in the adsorbing medium for longer duration actually helps in the formation of better monolayer. This question has been addressed in this thesis.

SAMs of alkanethiol were also formed on gold microelectrodes fabricated in our laboratory. The effect of different solvents on the structural integrity and barrier properties of SAMs were carried out using these SAM modified microelectrodes.

Thiocholesterol (TC) is a cholesterol molecule possessing a thiol moiety in place of a hydroxyl group at the 3- β position. A large number of molecular defects with a size of about 5-8 Å are present in TC monolayer on gold due to the size and irregular shape of the molecule, which is different from the defects observed in ordinary alkanethiol SAMs. This TC monolayer on gold acts as a nanoporous molecular assembly, exhibits microelectrode arrays behaviour and can be used for electroanalytical and biosensors applications. This SAM has a surface coverage of only 65-70%. We have investigated the structure and barrier property of TC SAM and utilized its low surface coverage for the formation of mixed monolayer and detection of copper ions.

Hopefully, the work which were carried out in this thesis will contribute to a better understanding of the nature, stability, structural integrity and different interfacial properties of SAMs.

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