



Characterisation of alkanethiol ($C_nH_{2n+1}SH$, $n = 3, 4, 6, 8, 10, 12$ and 18) self assembled monolayers by X-ray photoelectron spectroscopy

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Alkanethiol self assembled monolayers of varying chain lengths have been studied by X-ray photoelectron spectroscopy. Inelastic background of the S2p peak monotonically increases with the chain length. The binding energies and peak shapes are the same for all the samples studied indicating the chemical similarity of the monolayers. However, increased packing density is seen with hexane and octanethiol SAMs suggesting greater surface order. It is proposed that in higher and lower thiols, random orientation of the chains decreases packing density. Inelastic background of the S2p peak is directly proportional to the ellipsometric thickness of the monolayers. © 1998 Elsevier Science Ltd. All rights reserved

Introduction

For the past several years a large number of analytical tools have been applied to the study of self assembled monolayers.¹ Foremost among these tools are reflection-absorption infrared spectroscopy,²⁻⁴ contact angle measurements^{1,5} and ellipsometry.³⁻⁵ Electrochemical techniques have been extensively used in understanding electron transport dynamics in functionalised monolayers.⁶⁻⁹ Surface structure and adsorption geometry have been the topic of research using helium diffraction,¹⁰⁻¹² atomic force and scanning tunneling microscopies.¹³⁻¹⁸ Extensive body of literature has conclusively established that alkanethiols on gold form $(\sqrt{3} \times \sqrt{3})R30^\circ$ adlayer,^{13,16} although reports exist on the existence of other adsorbate geometries such as $p(2 \times 2)$ etc.^{14,15,17} Hexagonal arrangement of alkyl chains results in a near neighbour distance of 0.52 ± 0.03 nm and next nearest neighbour distance of 0.90 ± 0.04 nm respectively.¹³⁻¹⁶ Polarization dependent infrared spectroscopy has revealed the presence of tilt in monolayer assemblies which varies with the thickness and functionality.³

In spite of these investigations, one of the important surface analytical techniques, namely photoelectron spectroscopy has been applied only to a limited extent in characterizing self assembled monolayers.^{5,19-} Part of the reason being the very low intensity of the photoelectron features. The available studies of the photoelectron spectra of SAMs have concentrated on the surface characterization and the type of bonding at the head group-substrate interface.⁵ Both thiols and disulphides on gold

give a binding energy of ca. 162.5 eV for S2p corresponding to the Au^+S^- (gold thiolate) structure.^{21,23} In vacuum, the monolayers are stable to desorption up to a temperature of ca. 200°C.²³ The study of Bain *et al.*,³ on SAMs with a variety of functionalities showed that the terminal functionality is exposed to air. Monolayers of alkanethiols are resistant to adsorption and no adsorbate is detected even on prolonged exposure to air. While multiple sulphur binding sites are evident in the high resolution spectra²² and in the temperature programmed desorption,²¹ there is no such indication in the measurements using MgK_α radiation with and without monochromatisation. Poor signal intensity and the need to avoid surface damage due to high photon fluxes generally inhibit measurements at high resolution.

This paper describes an investigation of self assembled monolayers of alkanethiols ($C_nH_{2n+1}SH$) of varying chain length from $n = 3$ to 18. The results confirm the existing literature data. However, certain differences are noted. Firstly, it is suggested that the degree of order in the monolayer does not appear to be monotonically increasing with chain length, but has a maximum at $n = 6$ to 8. The increased packing density at these chain lengths is manifested in terms of increased coverage of sulphur. Corresponding effect is seen in the C1s spectra also. It appears that the disorder caused by the bent or misaligned alkyl chains in longer thiols could be the reason for their lower surface coverage. Secondly, the study illustrates the use of XPS in measuring the film thicknesses; data from XPS are almost in complete agreement with ellipsometry.⁴ Electron transport through the alkyl chains occur at a time scale faster than the photoelectron emission process, indicating tunneling across the monolayer chain. Even at an overlayer thickness of 25 Å, no surface charging is observed

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which is in agreement with electrochemical investigations. Within the resolution of the measurement, only one kind of sulphur binding site is observed suggesting the equivalence of adsorption sites on the surface. Other than the intensity variations, no change in the peak-width and position are observed with chain length. There is no direct information on the extent of order from XPS measurements.

Experimental

Propane, butane, octane and octadecane thiols were obtained from E. Merck and were used as such. Other thiols such as hexanethiol, decanethiol and dodecanethiol were prepared from the corresponding alkyl bromide using literature procedures²⁴ and were characterized using FTIR and TLC. Thermally evaporated gold films (1000 Å) deposited on polished glass substrates were used. To increase adhesion a 50 Å layer of Cr was pre-coated on glass. Scanning electron microscopic (SEM) studies showed that there are no pinholes or defects on the surface. Monolayers were prepared by immersing clean gold surfaces into a dilute solution of alkanethiol (1 mM) in ethanol.¹ The surfaces were kept in the solution overnight, washed with ethanol and characterized by X-ray photoelectron spectroscopy. Immersion time was the same for all the samples.

XPS analysis was done using a VG ESCALAB MkII spectrometer at a base pressure of 8×10^{-10} torr. The photoelectron spectra were measured with MgK_{α} radiation at an X-ray flux of 80 W which was kept low to avoid beam induced damage of SAMs. All the spectra were average of 10 scans of 60 s duration. The spectra were acquired with a pass energy of 20 eV for C1s and 100 eV for S2p. Survey scans were taken with a pass energy of 50 eV. The parameters such as electron take-off angle, X-ray flux, etc. were also kept constant for all the measurements. All the binding energies are referenced to Au $4f_{7/2}$ peak 84.0 eV.

Results and discussion

Monolayers of the type ($C_nH_{2n+1}SH$, $n = 3, 4, 6, 8, 10, 12$ and 18) have been characterized by ellipsometry, reflectance-absorption infrared spectroscopy, contact angle and X-ray photoelectron spectroscopy.^{4,5} The studies show that short and long chain thiol monolayers differ in structure. The long chain thiols form a densely packed, crystalline like assembly with fully extended alkyl chains whereas short chain thiol monolayer structures are disordered with lower packing density and coverage.

All the monolayers studied here show no oxygen or other contaminants in photoelectron spectra in conformity with previous reports. The monolayers exhibit no signs of deterioration in vacuum. At low X-ray fluxes, as used here, no desorption in the experimental time scale is observed. However, storage in the vacuum system for several days results in adsorbate coverage and the quality of XPS signals get affected. Acquisition time and duration of sample storage in vacuum were kept low to avoid minimum surface damage and contamination. As noted earlier⁵ the SAM surfaces are of lower surface energy than the clean gold film and no significant contamination occurs during the time-scale of the experiment. In Figure 1 we present the C1s X-ray photoelectron spectra of all the monolayers investigated. C1s manifests as a single line at 284.8 eV whose width does not change with monolayer thickness within the experimental uncertainty. This binding energy agrees with the reported binding energy of alkanethiol SAMs.^{5,19} Upon increasing the chain length the absolute intensity of the photoelectron spectrum increases which

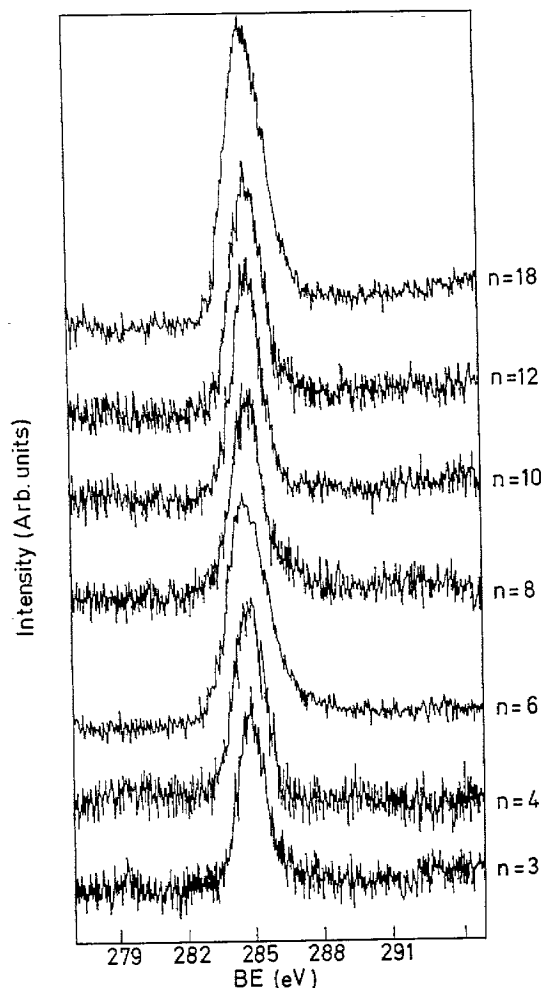


Figure 1. C1s spectra of seven monolayers of alkanethiols [$C_nH_{2n+1}SH$] on gold surface. (a) $n = 3$, (b) $n = 4$, (c) $n = 6$, (d) $n = 8$, (e) $n = 10$, (f) $n = 12$ and (g) $n = 18$.

is shown in Figure 2. An important aspect noted in Figure 1 is the increase in the inelastic background which increases as a function of chain length. Intensity of the inelastic background is proportional to the depth of the photoemission center, density of species above the center and the inelastically scattered electron

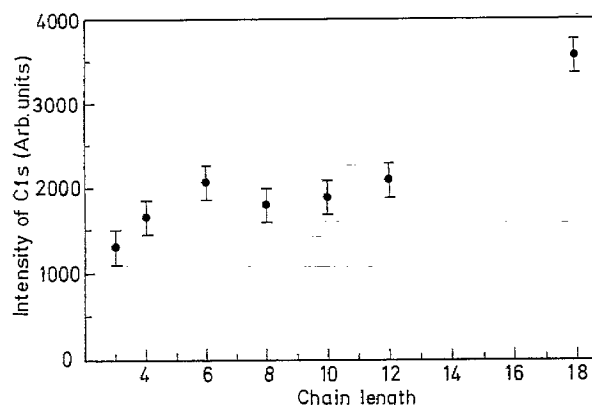


Figure 2. Plot of the variation of absolute intensity of C1s photoelectron peak with alkyl chain length.

excitation cross-section of the material.²⁵ In self assembled monolayers of this kind it can be assumed that the cross-section is a constant for various chain lengths. However, the depth of emission varies. The photoelectron mean-free path in materials of this kind is larger than 30 \AA ^{26,27} and therefore, in the present set of measurements all the carbon atoms contribute to the no loss photoelectron peak. Since the depth of photoelectron emission center varies, the increase in the inelastic background can not be linearly related to the thickness of the monolayer. Although a quantitative analysis of photoelectron intensities could reveal the true depth information, in the monolayers of this kind there is another easier approach (see below).

In Figure 2 it is observed that the intensity of C1s line is maximum at around $n = 6$. For smaller and higher chain lengths the intensity is lower than the expected values. This may be attributed to several reasons among which are partial desorption of the alkyl chains and increased randomness of the alkyl chains. The former possibility is not supported by S2p measurements (see below). Therefore it is suggested that increased disorder in larger chain length SAMs result in lower packing densities for the carbon chains which in turn cause the observed phenomenon. Decreased packing density can be because some of the alkyl chains are not fully stretched as suggested before.⁴ In the lower chain length regime, below $n = 6$ the self assembly is not complete as reported previously which results in lower packing density.

In Figure 3, S2p spectra of monolayers with various chain lengths are shown. As reported by Bain *et al.*,⁵ the S2p binding energy for thiolate sulphur is around 162.4 eV. Our spectrum although in agreement with Bain and Nuzzo,²¹ shows only one distinct sulphur species unlike that reported by Zubragel *et al.*,²² The S2p feature occurs at 162.2 eV binding energy in agreement with the $RS^- - Au^+$ nature of the coordination. Just as in the case of C1s intensity, S2p intensity is also maximum when $n = 6$ which again suggests the increased surface coverage of sulphur at this chain length. This can only be attributed to the increased order present at this chain length. It is important to note that in all the monolayers, nearly all the available surface adsorption sites are occupied initially.⁴ However, upon self organisation some sites desorb illustrating the competition of two effects namely the head group-surface chemisorption and lateral van der Waals interaction in the monolayer formation. In longer thiols inter-chain interaction dominate and only those surface sites which can support the ordered assembly are occupied. However, due to the presence of defects in the arrangement of alkyl chains, the hydrocarbon packing density is low. This results in the decreased intensity of C1s than the expected value. As a result of this, some of the available surface sites are not occupied by sulphur as well. In lower thiols, the sulphur atoms do not occupy all the available surface sites, because the alkyl chains are not ordered. For the in-between chain lengths the lack of orientational defects of the chains result in increased packing density. The presence of disorder in longer thiols could be due to shorter exposure times which needs to be investigated.

It may be noted that the inelastic energy loss background of the S2p peak continuously increases with thickness (Figure 3). Unlike in the case of carbon, here all the sulphur sites are immediately above gold and therefore the inelastic energy loss background should be directly proportional to the thickness assuming that the cross-section for inelastic scattering is the same for all the monolayers which is indeed reasonable. A plot of the increased inelastic background with chain length is linear showing this proportionality (Figure 4). In fact a plot of ellipsometrically

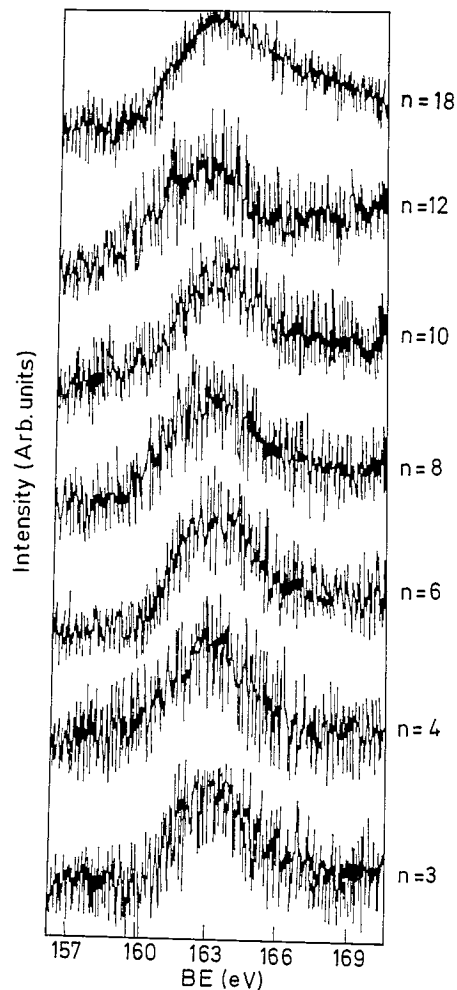


Figure 3. S2p spectra of seven monolayers of alkanethiol $[C_nH_{2n+1}SH]$ on gold surface. (a) $n = 3$, (b) $n = 4$, (c) $n = 6$, (d) $n = 8$, (e) $n = 10$, (f) $n = 12$ and (g) $n = 18$.

determined thickness with chain length also shows a similar slope. Ellipsometric thickness measured in the case of larger chain lengths is slightly lower than the XPS background intensity, indi-

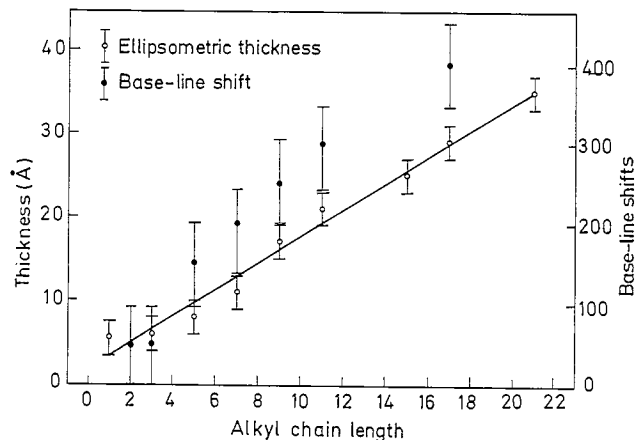


Figure 4. Plot of the variation of inelastic background of the S2p peak with alkyl chain length. The ellipsometrically measured thickness (from Ref. ⁴) is also shown for comparison.

cating that the density of the overlayer and the extent of order are important factors in determining the background intensity. If the background intensity is scaled to account for these effects, XPS background is a true measure of film thickness.

Conclusions

The present study has shown that the degree of order in monolayers of various chain lengths is maximum when n is around 8. As a result, the surface coverage of sulphur is increased slightly at this chain length. It is also evident from the study that monolayer thickness is a direct function of the inelastic energy loss background which is clearly demonstrated in the S2p spectra. In fact monolayer thickness can be calculated from a quantitative analysis of XPS data or the present data could be standardized using ellipsometric thickness. In all the cases, the binding energy is the same for all C1s and S2p, showing that surface charging is minimum in all the cases and tunneling is the dominant means of electron transport through the chains.

Acknowledgements

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