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# Measurement of molecular order and orientation in nanoscale organic films

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## Abstract

Self-assembled monolayers (SAMs) have, in recent years, attracted much interest for surface modification, surface coatings and as interfacial coupling agents. X-ray photoelectron spectroscopy (XPS) and carbon K-edge near edge X-ray absorption fine structure (NEXAFS) have been used to non-destructively measure the molecular conformation of organic films with thickness of the order of 1nm. Three different types of molecular conformation were found for γ-aminopropyltriethoxysilane (γ-APS) films formed on ZnO surfaces. The orientation of γ–APS films was observed to vary with adsorption time and surface coverage. Thus the molecular conformation of thin films can be controlled through adjustment of the application parameters.

*Keywords:* X-ray absorption spectroscopy; coatings; organic/inorganic interfaces; polycrystalline surfaces

## 1. Introduction

Self-assembled monolayers (SAMs) have, in recent years, attracted much interest for surface modification, surface coatings and as interfacial coupling agents [1,2,3]. γ-(aminopropyl)triethoxysilane (γ-APS) has, in particular, been of interest in a variety of applications such as biosensors [4] and anti-corrosion pretreatments [5]. Coupling agents with two moieties of different reactivities, as γ-APS possesses, will perform with an efficiency that varies with molecular conformation [1]. Other properties of organic SAMs are also affected by molecular conformation, for example, Dholakia et al [6] recently demonstrated that the current-voltage characteristics of oligo(phenylene ethynylyne) SAMs are significantly influenced by the orientation, packing and order of the molecules within the film.

Previous experiments in these laboratories have shown that the adsorption of γ-APS is complex [7]. Like its cousin propyltrimethoxysilane (PTMS), γ-APS undergoes *oscillatory adsorption* [8 – 12], whereby the molecules adsorb and attach strongly, yet after a time will tend to desorb and then are later able to re-adsorb. Further, γ-APS has also been shown to change its molecular orientation throughout the oscillatory adsorption isotherm [7].

X-ray photoelectron spectroscopy (XPS) is a powerful surface probing technique. X-rays illuminating a sample cause electrons to be ejected via the photoelectric effect. The intensity of peaks in the photoelectron spectrum corresponding to each element can be quantitatively analysed to give the composition, and the structure to some degree [13], of the sample surface.

Near-edge X-ray absorption fine structure (NEXAFS) is an experimental technique that involves probing a sample with X-ray radiation, whose energy is close to a known elemental absorption edge, and observing the degree to which the light is absorbed by the sample, which is usually achieved by measuring the resulting photoelectric effects. NEXAFS spectra consist of at least one step-like absorption edge, caused by photon induced excitations of core electrons to a continuum or quasi-continuum of final states, superimposed with a set of peak-like resonances that correspond with photo-excited electron transitions from core to anti-bonding, molecular or Rydberg states [14]. As such, NEXAFS spectra of a molecule provide a picture of the density of unoccupied states [14,15].

Carbon K-edge NEXAFS can be used to observe the bonding structures in carbon containing molecules through investigation of the core to antibonding state resonance peaks [14,15]. The intensity of these NEXAFS resonances vary with changes in the probing light beam's angle of incidence, or more correctly, with changes in the alignment of the corresponding final state of the resonance to the electric field vector of the probing light beam [14]. By observing the angular dependence of individual NEXAFS resonances, alignment effects in carbon containing molecules such as γ-APS may be deduced via the resonances of the propyl chain.

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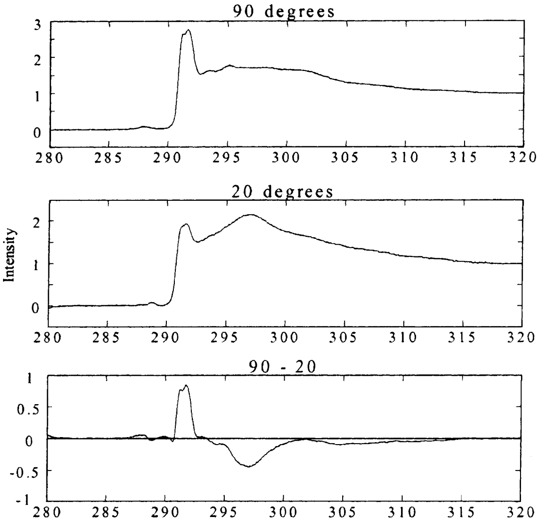

Fig. 1. C K-edge NEXAFS spectra of highly aligned octadecyltrimethoxysilane [16].

The alignment effects of long alkyl chain organosilanes have been studied extensively, with a number of investigations of the NEXAFS spectra of octadecyltrimethoxysilane (ODTMS) reported in the literature [16,17]. ODTMS films tend to align with the alkyl chains perpendicular to the substrate surface plane. The resulting NEXAFS spectra show a strong C-H* resonance at 292eV for 90° incidence and a broader, strong C-C* resonance at 297eV for 20° incidence. 90°-20° difference spectra for an ODTMS SAM shows a strong positive peak at 292eV and a strong negative dip at 297eV [16]. For alkyl chains lying flat against the substrate surface, these peaks and dips in the difference spectra would be reversed in sign.

In this paper, we report studies of the much shorter γ-APS molecule and show that the alignment of this molecule is a strong function of adsorption time and surface coverage.

## 2. Experimental

Polycrystalline zinc sheet (of purity 99.99%) was obtained from Goodfellow Cambridge Ltd. (Cambridge, England). γ-(Aminopropyl)triethoxysilane (γ-APS), $NH_2CH_2CH_2CH_2Si(OCH_2CH_3)_3$ (of purity 98%) was supplied by the Aldrich Chemical Co., Inc. (Milwaukee, WI). Solutions of 1% concentration by volume and natural pH (10.4) were prepared by stirring the required quantity of γ-APS into deionized (5 μS MilliQ) water for a period of 5 min, by which time the γ-APS had dissolved completely and was considered to be fully hydrolysed. For adsorption at lower pH (6.4), the solutions were acidified with acetic acid. The metal surfaces were all prepared by abrading lightly with 1200 grade abrasive paper and then etched ultrasonically for 1 hour in pH 3.0 acetic acid solution, rinsed in deionized (5μS MilliQ) water and allowed to air-dry prior to dip coating. Once dipped, samples were blown dry with nitrogen and stored under a nitrogen atmosphere to prevent reaction of amine groups with $CO_2$ in air to form ammonium carbamates [1].

Angle resolved NEXAFS spectroscopy experiments were carried out, using total electron yield mode (TEY), on the 2B1 beam line at the synchrotron of the Pohang Accelerator Laboratory (PAL), Pohang, Korea. An UHV chamber was attached at the end of the beam line, which had a working pressure that was typically 3 – 5 x $10^{-10}$ mbar. NEXAFS spectra were recorded at angles of 20° and 90°, measured between the direction vector of the incident linearly polarised light and the surface plane of the sample. All NEXAFS spectra have been normalised through division by a clean reference sample, as discussed by Watts et al [18].

## 3. Results and Discussion

XPS experiments in our laboratories at the University of Newcastle have shown orientation effects in γ-APS thin films on zinc oxide [13]. Measured Si:N ratios differing from the stoichiometric value of 1 are indicative of the preferential adsorption to the ZnO surface by either the amine (high Si:N) or silanol (low Si:N) functional groups. These experiments show that the molecular orientation of the γ-APS film depends on the pH of the dipping solution relative to the isoelectric point of the substrate, which for ZnO is about 9.

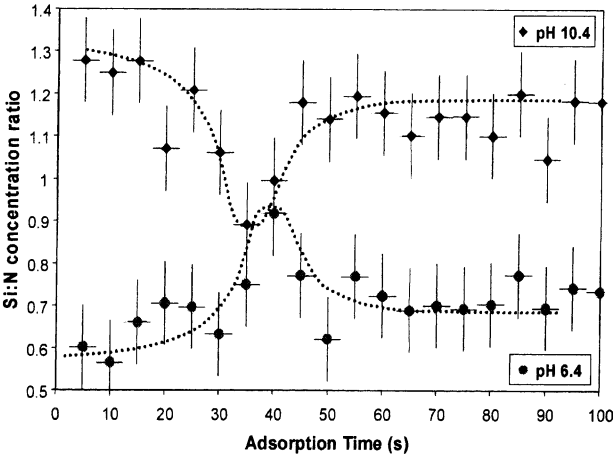

Fig. 2. The measured XPS Si:N ratio of γ-APS films on zinc oxide surfaces at two dipping pH values as a function of dip time. [13]

However, there still remains some ambiguity about the way that the two curves in Fig. 2 converge at 40s dip time. At this point, the molecular orientation could be upright with an equal number of molecules adsorbing via the amine as via the silanol functional group, completely random, or the molecules could be lying flat against the substrate. Therefore NEXAFS spectra were collected in order to understand the changes in molecular conformation as a function of time, with a particular focus upon an adsorption time of 40 s.