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Surface chemistry of the iron tetraazamacrocyclic on the aminopropyl-modified surface of oxidized n-Si(100) by AFM and XPS

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The structure and formation mechanisms of 3-aminopropyltrimethoxysilane (3-APTS) films deposited on wet-chemically grown silicon dioxide over n-Si(100) wafer have been examined systematically using x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The asymmetric N 1s XPS spectrum for the anchored 3-APTS was fitted for $-\text{NH}_2$ (399.6 ± 0.3 eV) and $-\text{NH}_3^+$ (401.1 ± 0.3 eV). Rougher surfaces are obtained by deposition from toluene solutions than from the gaseous phase. Over the 3-APTS layer was deposited the $[\text{FeTIM}(\text{CH}_3\text{CN})_2]^{2+}$ complex, where TIM is 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene. The adsorption occurs by acetonitrile replacement for the $-\text{NH}_2$ -grafted group with the equatorial plane parallel to the organomodified surface. Once FeTIM can bind a CO, NO or N-heterocycle, a built-on Si wafer sensor device could be envisaged for these molecules. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: 3-aminopropyltrimethoxysilane thin films; silicon dioxide; AFM; XPS; TIM; iron tetraazamacrocyclic

INTRODUCTION

A great variety of organoalkoxysilanes have been used in the chemical modification of surfaces of various metal oxides.^{1,2} These compounds usually consist of three alkoxide groups at one extremity, of which one or more groups can be hydrolysed and subsequently bound to the surface. The other extremity is typically an organofunctional group, which can be bound to any of a variety of ligand units acting as Lewis bases. This modification strategy has wide applications, including the preparation of hydrophobic surfaces,^{3,4} stationary phases for reverse-phase chromatography^{5,6} and the design of biocompatible surfaces^{7,8} and sensors.^{9,10}

In this paper, we report on the organomodification of wet-chemically grown SiO_2 layers on n-type Si(100), hereafter referred to as SiO_2/Si , using 3-aminopropyltrimethoxysilane

(3-APTS) for subsequent grafting of the $[\text{FeTIM}(\text{CH}_3\text{CN})_2]^{2+}$ complex (hereafter named FeTIM, where TIM is 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; see Fig. 1). This FeTIM complex is a versatile molecule very similar in structure to the more complex porphyrins and phthalocyanines, showing interesting ability to bind CO, NO and N-heterocycle molecules such as imidazole derivatives.^{11,12,13} Furthermore, this macrocycle complex not only binds these molecules in solution but, based on its thermodynamic stability constants, also can be selective; based on kinetic studies, the binding is reversible. Thus its adsorption on silicon surfaces could be used for bioanalyte sensor design.

In order to characterize the adsorbed species on the SiO_2/Si surface we have used XPS, which is one of the principal tools used in the analysis of organic mono- and multilayer systems supported in solids.¹⁴ However, great care has to be taken when analysing organic substrates by XPS. Wang and Craig¹⁵ investigated the stability of a trimethylsilane film grown on the Si(100) surface, as well as the chemical environment of the elemental constituents, and demonstrated that organosilane compounds are sensitive to x-ray beams. Therefore, when studying silane films it is necessary to verify their stability regarding the analytical procedure.

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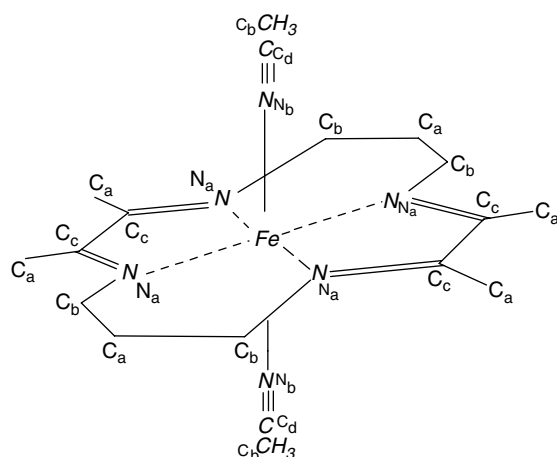


Figure 1. Sketch of the $[\text{Fe}(\text{TIM})(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ complex.

We employed atomic force microscopy (AFM) to understand better the growth mechanism of the films and to know the film morphology at every preparation step. This technique has proved to be instrumental in characterizing similar systems.¹⁶

EXPERIMENTAL

Substrate and reagents

Plates of 1 cm² were cut from Si(100) wafers (Goodfellow Cambridge Ltd). The chemicals used in this work were: 98% 3-APTS (Aldrich), 40% HF (Synth), 30% H₂O₂ (Mallinkrodt), toluene (Mallinkrodt), 24% NH₄OH (Mallinkrodt), 98% H₂SO₄ (Mallinkrodt) and deionized water (18.2 MΩ cm⁻¹). All reagents were used as received, except for toluene, which was distilled and stored in a flask containing molecular sieves (4 Å) to prevent water absorption. The $[\text{Fe}(\text{TIM})(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ has been prepared by the template method described by Reichgot and Rose.¹¹ Proton nuclear magnetic resonance (¹H-NMR), elemental analysis (C,H,N), and electronic absorption spectroscopy in the ultraviolet-visible region (UV-Vis) were used to check the chemical composition and purity. The results for ¹H-NMR (CDCl₃) were: α-CH₂ (4.07 ppm), β-CH₂ (2.14 ppm) and CH₃ (2.65 ppm); λ_{max} = 551 nm (ε = 8 × 10³) and other peaks at 514–492 nm in agreement with literature data.¹³

Silicon wafer preparation

Prior to the organomodification of silicon, cleaning in 10% (v/v) HF solution for 15 s at room temperature to remove the native oxide and then a three-step oxidation were carried out: H₂SO₄/H₂O₂ (3:1, v/v) at 100 °C for 2 h; NH₄OH/H₂O₂ (1:1) ultrasonically at room temperature for 30 min; and H₂SO₄/H₂O₂ (3:1) ultrasonically at room temperature for 15 min. After each one of these steps the plates were washed with deionized water (18.5 MΩ⁻¹ cm resistivity). This procedure was optimized from the literature procedures^{14,17} to obtain smooth and clean surfaces of SiO₂/Si.

Argon sputtering using BALTEC Med 020 sputtering equipment was done to give gold-covered SiO₂/Si wafers.

The Au layer thickness of 20 nm has been measured by a quartz crystal microbalance.

Organosilane film preparation

The organosilane was adsorbed under a dry nitrogen atmosphere by two distinct methods: liquid- and gas-phase adsorption. In liquid-phase adsorption the SiO₂/Si plates were immersed directly in toluene solutions of the 3-APTS at 298 K. The adsorption of 3-APTS was performed in 3.0 mM and 0.9 M toluene solutions. In order to obtain the optimum immersion time for deposition of a high surface coverage of 3-APTS, the surface coverage was measured by XPS N/Si atomic ratio as a function of time for the 0.9 M 3-APTS solution.

In the gas-phase method, the organosilane and the SiO₂/Si plate were kept in separate 10 ml flasks and both flasks were placed inside a chamber filled with dry nitrogen. Pumping the chamber with a rotary vacuum pump for 2 min caused the organosilane to evaporate and fill the entire chamber. The organosilane vapour was kept in contact with the SiO₂/Si wafer for 2.5 h.

Subsequent to initial layer deposition, for both methods the plates were washed ultrasonically with toluene for 15 min in order to remove the physically adsorbed silane overlayer and then dried under a dry nitrogen flux at room temperature.

The adsorption of FeTIM from 1.0 mM acetonitrile solution under a nitrogen atmosphere over SiO₂/Si or Au/SiO₂/Si films was done by immersing the plates in the solution for 15 min. The adsorption time was inferred from the solution dissociation rate constant of the bis-acetonitrile complex in acetonitrile solution: $k_{\text{acetonitrile}} = 195 \text{ s}^{-1}$.¹⁸ Before FeTIM adsorption, the organomodified plates were washed ultrasonically with acetonitrile to check for the absence of 3-APTS desorption. No desorption was observed by XPS and AFM.

Atomic force microscopy

The AFM technique was used to access the very smooth surface morphological modification in the order of tenths of nanometres due to the adsorption process over the substrates.

The AFM experiments were carried out with a NanoScope IIIa from Digital Instruments. To minimize surface deformation and material removal, the experiments were performed in intermittent contact mode (Tapping ModeTM) using a silicon cantilever with a spring constant of ~70 N m⁻¹ at a scan rate of 1 Hz. All measurements were done under air at room temperature, employing the root-mean-square roughness (*R*_{rms}) to compare the surfaces in a quantitative manner and evaluate the morphological changes on the plates.¹⁹ Because the roughness value depends on the observation scale, all experiments were carried out on a scale of 1 μm.

X-ray photoelectron spectroscopy

The XPS analysis was performed to assess the adsorption rates of the organosilanes as well as to characterize the chemical species on the surface.

The organomodified wafers prepared at 0.9 M with varying immersion times were analysed with a Kratos XSAM

HS spectrometer using non-monochromatic Mg K α radiation (1253.6 eV, 180 W). The base pressure in the chamber was in the range of 5×10^{-7} to 1×10^{-6} Pa. The binding energy correction was done using Si 2p at 103.5 eV for SiO₂.²⁰ No flood gun was used.

The other XPS measurements were carried out with an Omicron spectrometer using non-monochromatic Al K α radiation (1486.6 eV, 180 W). The base pressure in the chamber was in the range of 5×10^{-7} to 1×10^{-6} Pa.

The spectra were charge corrected using the [PF₆]⁻¹ P 2p peak set at 136.7 eV for the FeTIM non-grafted complexes. The low P 2p signal, or its absence, in the case of FeTIM grafted on organic molecules brought about the need to use the [PF₆]⁻¹ F 1s peak for the FeTIM films and/or the SiO₂ Si 2p peak at 103.3 eV for the organosilane films. Fluorine was used as a secondary reference because its binding energy was obtained from the F 1s core level of the [FeTIM(CH₃CN)₂](PF₆)₂ complex. For the FeTIM films, both Si 2p and F 1s references gave the same corrected binding energies. For a cross-check of the binding energy calibration procedure, a thick film of FeTIM adsorbed from acetonitrile solution on the Au/SiO₂/Si surface was analysed; all the former charge correction procedures were carried out and the results compared with the correction value obtained by using Au 4f peaks. All the procedures yielded the same charge correction factor of 2.5 ± 0.2 eV.

The chemical compositions of all samples were verified by comparison between the elemental analysis data and the theoretical formula for covalent-grafted parent compounds, and also by atomic ratios obtained using XPS according to

$$\frac{N_a}{N_b} = \frac{A_a \sigma_b}{A_b \sigma_a}$$

where A is the peak area for elements a and b , σ is the photoionization cross-section²¹ for elements a and b and N is the atomic concentration of elements a and b . All atomic ratios were calculated at a take-off angle of 90° (from the surface plane) and a magic angle of 54.7° (photoincident-to-electron take-off angle), unless stated otherwise.

The accuracy for the atomic ratio values is $\pm 10\%$, and for the binding energy is ± 0.2 eV, except for Fe 2p in the FeTIM complex, in which case the accuracy is $\pm 15\%$ for the atomic ratios and ± 0.3 eV for the binding energy.

All XPS peaks of the elements in insulating samples were fitted using Gaussian–Lorentzian peaks with at least an 85% Gaussian contribution and the fitting procedure follows Leclercq and Pireaux procedures.²²

RESULTS AND DISCUSSION

The XPS spectra of the oxidized samples (not shown) did not feature SO₄²⁻ S 2p or NH₄⁺ N 1s peaks of the sulphuric acid and ammonium hydroxide used in the oxidizing procedure. The F 1s photoemission peak was detected after HF treatment at very low surface concentration: F/Si atomic ratio of 0.11. The F 1s peak disappears after oxidation. Table 1 shows the same R_{rms} value of 0.2 nm for the HF etched substrate and oxidized silicon wafer. Because the R_{rms} value obtained is quite small, the surfaces are almost atomically flat. This

Table 1. Root-mean-square roughness (R_{rms}) for the different surfaces obtained by AFM (tapping mode, 1 μm scale)

Sample	R_{rms} (nm)
Cleaned silicon	0.2
Oxidized silicon	0.2
3-APTS (from gas phase)	4.2
3-APTS (from 3 mM toluene solution)	14.2
3-APTS/FeTIM (on gas-phase 3-APTS)	1.5
3-APTS (on 3 mM 3-APTS solution)	0.7

R_{rms} value is in agreement with data reported by Kawabata and Adachi²³ and Maida *et al.*²⁴ It turns out that the chosen procedure using about six to ten times the HF concentration and a shorter exposure time (10 s versus 180–300 s) gave a satisfactory roughness result.

Taking successive elemental XPS spectra of the 3-APTS organomodified surfaces over the total acquisition time and comparing their shape as well as N/Si atomic ratios (not shown), no decomposition was observed.

The adsorption of 3-APTS from 0.9 M toluene solution showed a wide N 1s photoemission peak that could be well fitted to two Gaussian–Lorentzian functions components with 399.6 eV and 401.2 eV binding energies and areas of 74% and 26%, respectively, of the total N 1s peak area. The N/Si atomic ratio obtained was 0.86, resulting in a nitrogen surface atomic concentration of 5.4%. The 399.6 eV peak is observed at higher binding energy than the values reported in the literature (399.3 eV for similar layers^{17,25}), indicating that probably the –NH₂ group is interacting with other groups by hydrogen bonding. The AFM image of this sample (not shown) gives us a very rough surface covered with agglomerates of 200–700 nm in diameter. It turns out that probably the 3-APTS is forming agglomerates in the bulk of the liquid phase, and it is known from ²⁹Si-NMR and Fourier transform spectroscopy studies that polymerization to form siloxane bonds between adsorbing species often accompanies surface adsorption.^{26,27} Indeed, Shimizu *et al.* have reported that 3-APTS forms micelles in toluene solution: NMR measurements of critical micelle concentration estimated a value of 0.47 M.²⁶ Therefore, we shift our attention to the more dilute solutions (3.0 mM) in order to obtain flatter and more organized modified surfaces.

We performed a time-dependent adsorption study in order to obtain the best silane adsorption time for 3 mM toluene solutions. This study was based on the N/Si atomic ratios of the 3-APTS on the SiO₂/Si surface. The time-dependent study of adsorption of 3 mM silane showed N/Si atomic ratios of 0.13, 0.21 and 0.24 for 30, 75 and 150 min, respectively. Therefore, there is a tendency towards a constant atomic ratio after 150 min, and this time was used for further studies. The XPS spectra measured at two take-off angles (90° and 45° from the surface plane) for the 150 min adsorption showed that the N/Si ratios are the same (0.23

and 0.24, respectively), indicating that probably the 3-APTS is forming a non-ordered film on the SiO₂/Si surface. Also, the N/Si ratio is smaller than that obtained for the 0.9 M solution (N/Si = 0.86), showing that the bonding of the surface is through a different mechanism than would be expected from the solution behaviour described by Shimizu.

The N 1s spectra for the grafted 3-APTS showed an asymmetric and wide peak that was fitted by two components: one attributed to -NH₂ (399.9 eV) and the other to -NH₃⁺ (401.0 eV). For the samples with higher N/Si ratios, only one peak was observed at the lowest binding energy side. This fact is in agreement with the proposed growth model, i.e. a smaller N/Si ratio film corresponds to a film close to a monolayer. In this case, the amine groups would be interacting with the surface silane groups withdrawing their protons²⁸ and causing the appearance of the peak due to protonic species at a higher binding energy. As the film covers the surface and the film thickness is increased, the interaction between the amine groups and the surface silanol groups no longer occurs.

The gas-phase 3-APTS SiO₂/Si surface showed an N 1s XPS spectrum [Fig. 2(a)]. The two peaks at 399.7 and 402.0 eV were assigned to the same species as discussed before. The N 1s total peak area percentage was 83% and 17%, respectively, for a take-off angle of 90°. These values are close to the values obtained for the surface modified with 3.0 mM toluene solution after 30 min of adsorption. The N/Si atomic ratios are very similar also—0.13 for adsorption from a 3.0 mM solution at 30 min and 0.10 for adsorption from the gaseous phase—so the films appear very similar chemically. The N 1s XPS spectrum for the gas-phase modified sample at a take-off angle of 45° [Fig. 2(b)], showed an increase in the N/Si atomic ratios (0.20) but the binding energy values did not change. Because the nitrogen in an 3-APTS ordered layer would be on top of the modified surface, we should see a higher N/Si atomic ratio at lower take-off angles. This is in agreement with the adsorption model of siloxane bonds and surface-oriented amino groups. However, the presence of -NH₃⁺ species indicates that the surface is not totally covered by the 3-APTS and that we have some silanol groups remaining, which, by interaction with the -NH₂, gives rise to NH₃⁺ groups. The ratio between protonated and non-protonated amino species for the 3-APTS gas-phase modified surface increases dramatically at the 45° take-off angle [Figs 2(a) and 2(b)], showing that the -NH₃⁺ groups are concentrated at the top layer of the surface and that the -NH₂ groups are deeper, on average. The -NH₂ groups probably are interacting with other silanol groups by hydrogen bonding, explaining the high binding energy values compared with other examples from the literature data (399.7 vs. 399.3 eV).^{17,25}

The adsorption of the 3-APTS by both procedures (solution and gas phase) caused an increase in the roughness as measured by AFM (see Table 1). The increase in the roughness for liquid (solution)-phase adsorption is in agreement with the adsorption model based on XPS as discussed above. The *R*_{rms} of the surface organomodified using gas-phase adsorption indicated a smoother surface than that prepared by the solution adsorption. This difference

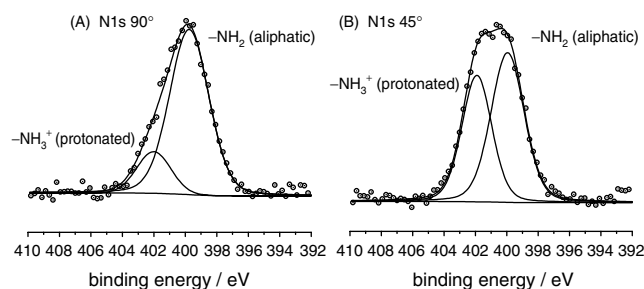


Figure 2. The XPS spectrum in the N 1s photoemission peak region of the Si/SiO₂ surface after adsorption of 3-APTS from 3 mM toluene solution at take-off angles of 90° (a) and 45° (b).

in the roughness was attributed to the formation of clusters in solution and to the silane polymerization near the surface and its later adsorption on the SiO₂/Si surface, even for the silane in diluted concentration. In the gas phase, the silane would be expected to form dimers at most, which would be adsorbed in a more ordered way resulting in a smoother surface.

Figure 3(a) displays the FeTIM film over an Au/SiO₂/Si wafer using a wide-scan XPS spectrum, which contains all the characteristic lines of the elements in the complex and substrate. The C 1s and N 1s binding energies are shown in Table 2, with respective assignments according to Fig. 1 labelling.

We used the photoelectron lines of model compounds reported in the literature for curve fitting the FeTIM spectra (Table 2). The binding energy values for the iron coordinated to the acetonitrile were estimated based on the respective adduct with BF₃.²⁹ The binding energies for C_a and C_b (see Fig. 1) were estimated from 1-propylamine coordinated to BF₃. The peaks corresponding to C_c and N of the macrocycle were estimated from the imine group in the 2,6-dimethylpyridine adduct with BF₃.²⁹ The metallic ion and the strong Lewis acid BF₃ are expected to present a

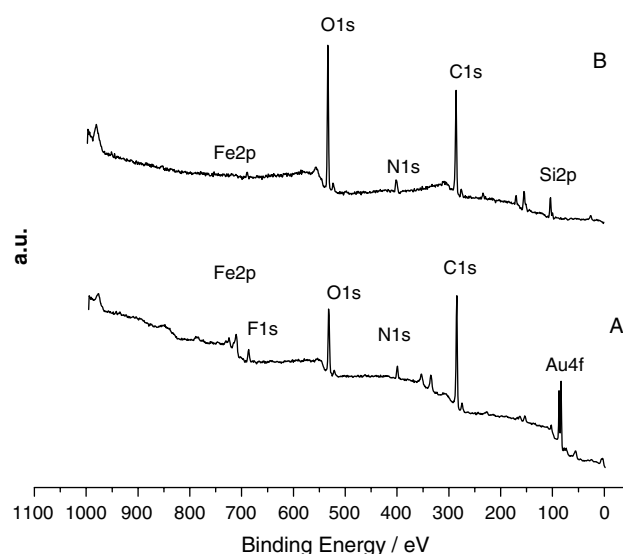


Figure 3. The XPS long-scan spectra of: (a) [Fe(TIM)(CH₃CN)₂](PF₆)₂ complex over Au film sputter deposited on n-Si(100); (b) FeTIM adsorbed over 3-APTS layer adsorbed from the gaseous phase over SiO₂/Si wafer.

Table 2. The C 1s and N 1s binding energies and atomic ratios for the $[\text{Fe}(\text{TIM})(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ complex

Peak ^a	BE (eV)	% Area ^b	Ref.
C 1s C _a	285.2	35.0 (33.0)	This work
C _b	285.4	21.0 (22.0)	This work
C _c (imine-Fe + CH ₃ *-CN-Fe)	286.6	35.0 (33.0)	This work
C _d (CH ₃ C*N-Fe + amine-Fe)	288.6	8.2 (11.0)	This work
CH ₃ *CNBF ₃	287.5		21
CH ₃ C*NBF ₃	289.3		16
CH ₃ *CH ₂ NH ₂ BF ₃	285.6		16
CH ₃ CH ₂ *NH ₂ BF ₃	287.0		16
C ₅ H ₅ NBF ₃	286.3		16
2,6-(CH ₃ *) ₂ C ₅ H ₅ N	285.4		16
N 1s			
N _a (C≡N)	399.8	67.0 (67.0)	This work
N _b (C≡N)	401.2	33.0 (33.0)	This work
CH ₃ CNBF ₃	402.0		20
C ₅ H ₅ NBF ₃	401.6		20

^a The asterisk indicates the carbon for which the binding energy is shown.

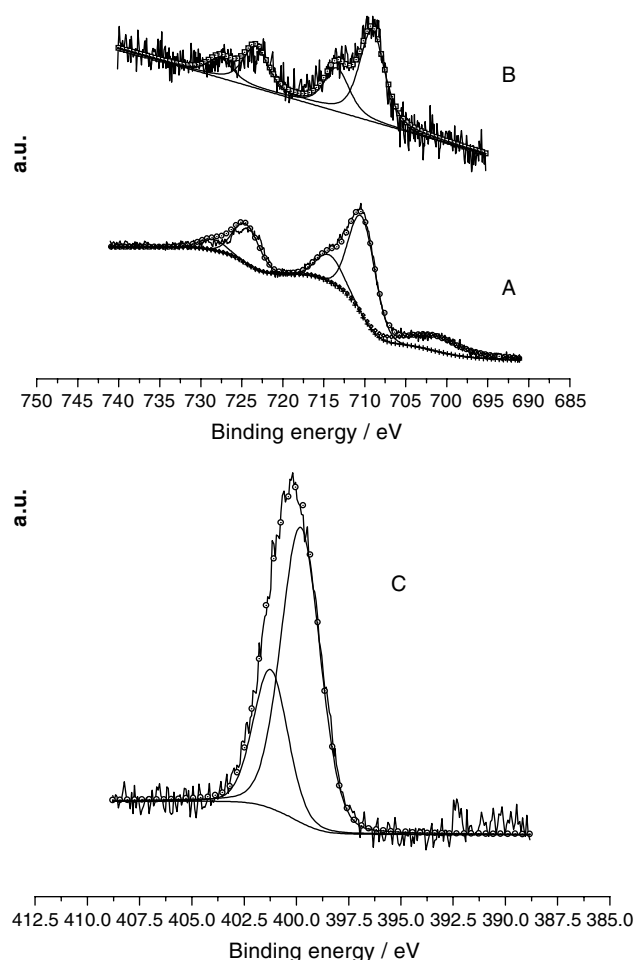
^b Theoretical value in parentheses.

similar behaviour on the nitrogen atomic electronic density, except for the fact that d⁶ low-spin metals such as Fe (II) also participate in backbonding interactions with π acid ligands such as nitriles and diimine groups (C≡N). Therefore, we would expect to see the N 1s and C 1s (C_c and C_d) peaks to appear at slightly smaller binding energy than those reported for the adduct with BF₃ (see Table 2 and Fig. 4(c) for N 1s peaks). Indeed, this is observed, confirming the π acid behaviour of the TIM and acetonitrile.

The results displayed in Table 2 show reasonable agreement for the atomic ratios of C and N obtained by XPS (within 0.29) for the different species compared with those estimated from the complex chemical formula (within 0.33). Therefore, we can infer that the complex did not decompose by x-ray exposure.

The Fe 2p photoelectron peak region [Fig. 4(a)] shows two broad asymmetric peaks fitted to two doublet peaks with 2p_{3/2} peak binding energies at 710.3 and 714.3 eV and spin-orbit splittings of 13.8 and 14.3 eV. The spin-orbit doublet area ratios were 0.4 for both. The first binding energy value and its spin-orbit splitting is in agreement with the value observed for iron(II) in the poly(μ -1,4-diisocyanobenzene)octacyanophthalocyanate iron(II) complex.³⁰ However, this lower binding energy value has been used already to characterize iron(III) in the 'hinged' iron porphyrins adsorbed on the n-CdSe(0001) surface.³¹

Indeed, in its system the authors claim that the semiconductor surface could push electronic density in the porphyrin system and this could explain the lower binding energy of the iron(III) porphyrin system. In our case, we propose that because the ligands bound to the iron core are π acid in nature they shift electronic density from the metal, thus increasing the measured binding energy. Also, the spin-orbit splitting

**Figure 4.** The Fe 2p and N 1s XPS spectra of $[\text{Fe}(\text{TIM})(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ (a,c) and the Fe 2p spectrum of FeTIM adsorbed on the 3-APTS layer adsorbed from the gaseous phase on SiO₂/Si (b).

is quite close to the reported value for Fe(II).³² The second doublet with higher Fe 2p binding energies is probably due to the presence of some Fe(III)TIM complex because both the high binding energy and spin-orbit splitting are close to those of Fe(III) systems.³³ It is important to note that electron paramagnetic resonance or electronic spectroscopy observed no oxidation product in the adsorption solutions or FeTIM complex powder during 3 days in air. From this we infer that oxidation of the surface-bound FeTIM took place due to reaction of the film with air. Because no oxidation of the FeTIM powder could be observed previously by other surface non-specific techniques, this implies a different reactivity for the surface-bound FeTIM compared with the bulk FeTIM. Iron(III)TIM complexes also have been isolated and characterized for CO and SCN⁻¹ ligands and detected in solution for thiolate ligands.³⁴

Based on solution kinetic data for acetonitrile replacement by neutral amines, available in the literature¹⁸ for $[\text{Fe}(\text{TIM})(\text{CH}_3\text{CN})_2]^{2+}$ and in our studies in solution by absorption spectroscopy in the visible region for FeTIM in the presence of ten times more concentrated 3-APTS (not shown), we expect facile substitution of one acetonitrile by the -NH₂ group of the grafted 3-APTS. This 3-APTS binding to FeTIM in solution causes a strong red shift in λ_{max}

for the metal-to-ligand charge transfer (MLCT) band peak position ($C=N\ p\pi \leftarrow Fe\ d\pi$) from 552 to 623 nm. This shift is indicative of coordination of 3-APTS to the metal and a resulting decrease in the electron affinity of the Fe $d\pi$ orbitals as a π -backbonding ligand is replaced by a simple σ -donor.

After adsorption of the FeTIM we are able to identify almost all the photoemission peaks from the elements in the sample [Fig. 3(b)], indicating efficient binding of the macrocycle on the 3-APTS adsorbed on the SiO_2/Si (P 2p peaks are not present due to its lower cross-section). There are two broad Fe 2p peaks [see Fig. 4(b)] that are very similar in shape to the original complex spectrum [Fig. 4(a)]. However, the Fe 2p_{3/2} lines of the organomodified plate are at 709.1 eV (Fe1) and 713.4 eV (Fe2), with the same spin-orbit splitting as that before adsorption on 3-APTS and with a respective Fe1/Fe2 area ratio of 2:1. The shift to lower binding energy for the 3-APTS-modified surface is strong evidence of binding because the primary amine-like 3-APTS on the surface should be a better σ -donor and would have no π -backbonding ability. Analysis of the other photoemission peaks is rather complicated due to the overlap of imine, acetonitrile and coordinated amine N and C 1s peaks and 3-APTS non-coordinated groups.

We noted also a decrease in the AFM R_{rms} roughness value after FeTIM adsorption (see Table 1), suggesting that the FeTIM complex was adsorbed with its equatorial plane parallel to the surface, in agreement with XPS data showing $N_{surface}-Fe$ bonding.

CONCLUSIONS

The structure and the film formation process of 3-APTS over SiO_2/Si were investigated by AFM and XPS. Adsorption of 3-APTS from 0.9 M toluene solution results in rough surfaces, probably due to adsorption of micellar and polymeric species on the surface. The results suggest that the smoothest surfaces from solute adsorption are obtained at an optimal adsorption time of ~150 min from a 3 mM toluene solution at room temperature. The surfaces obtained by adsorption from the gas ($R_{rms} = 40\text{ \AA}$) phase are smoother than adsorption from 3 mM solutions (140 \AA) of 3-APTS, which are smoother than adsorption from 0.9 M solution. These results suggest that the most important aspect of the experimental procedure to be tuned is to avoid the formation of agglomerated species from the adsorption media: gas or liquid phase. Therefore, gas-phase adsorption is more effective for growing thin films. In films with lower N/Si ratios, the amine groups ($-NH_2$) interact with the silanol groups ($-OH$) of the oxidized surface, with a tendency to result in protonated species ($-NH_3^+$) on the topmost surfaces. The XPS spectra of the FeTIM has allowed us to infer aspects of the bonding features in the system, especially regarding the acetonitrile and TIM bonding modes. Adsorption of the FeTIM compound occurs with the equatorial plane parallel to the surface, probably through the formation of N-Fe covalent bonds, and in this case the grafted $-NH_2$ would have replaced one acetonitrile group.

Once FeTIM has been adsorbed on the surface, we intend to study its reactivity against bioanalyte molecules such as CO, NO or N-heterocycles, envisaging its application as sensors for such analytes.

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REFERENCES

- Mirkhalaf F, Whittaker D, Schiffrin DJ. *J. Electroanal. Chem.* 1998; **452**: 203.
- Cao C, Fadeev AY, McCarthy TJ. *Langmuir* 2001; **17**: 757.
- Tada H, Nagayama H. *Langmuir* 1994; **10**: 1472.
- Sagiv J. *J. Am. Chem. Soc.* 1980; **102**: 92.
- Sander LC, Wise SA. *Crit. Rev. Anal. Chem.* 1987; **18**: 299.
- Regnier FE, Unger KK, Majors RE. *J. Chromatogr.* 1991; **R9**: 544.
- Stenger DA, Hickman JJ, Calvert JM. *J. Am. Chem. Soc.* 1992; **114**: 8435.
- Zhang MQ, Desai T, Ferrari M. *Biomaterials* 1998; **19**: 953.
- Allara DL. *Biosens. Bioelectron.* 1995; **10**: 771.
- Ross CB, Sun L, Crooks RM. *Langmuir* 1993; **9**: 632.
- Baldwin DA, Pfeifer RM, Reichgot DW, Rose NJ. *J. Am. Chem. Soc.* 1973; **95**: 5152.
- Butler A, Linck RG. *Inorg. Chem.* 1984; **23**: 2227.
- Chen Y, Sweetland MA, Shepherd RE. *Inorg. Chim. Acta* 1997; **260**: 163.
- Frydman E, Cohen H, Maoz R, Sagiv J. *Langmuir* 1997; **13**: 5089.
- Wang PW, Craig JH Jr. *Nucl. Instrum. Methods Phys. Res. B* 1998; **141**: 223.
- Wei ZQ, Wang C, Zhu CF, Zhou CQ, Xu B, Bai CL. *Surf. Sci.* 2000; **459**: 401.
- Harder P, Bierbaum K, Woell Ch, Grunz M. *Langmuir* 1997; **13**: 445.
- Hamilton DE, Lewis TJ, Kildahl NK. *Inorg. Chem.* 1979; **12**: 3364.
- Dunaway DJ, McCarley BL. *Langmuir* 1994; **10**: 3598.
- Moulder JF, Sticke WF, Sobol PE, Bombem KD. *Handbook of X-Ray Photoelectron Spectroscopy*. Perkin-Elmer: Eden Prairie, MN, 1992.
- Scofield JH. *J. Electron Spectrosc. Relat. Phenom.* 1976; **8**: 129.
- Leclercq G, Pireaux J-J. *J. Electron Spectrosc. Relat. Phenom.* 1995; **71**: 141.
- Kawabata Y, Adachi S. *Appl. Surf. Sci.* 1999; **152**: 177.
- Maida O, Yamamoto H, Okada N, Kanashima T, Okuyama N. *Appl. Surf. Sci.* 1998; **130**: 214.
- Bierbaum K, Kinzler M, Wöll Ch, Grunze M, Hähner G, Heid S, Effenberger F. *Langmuir* 1995; **11**: 512.
- Shimizu I, Okabayachi H, Hattori N, Taga K, Yoshino A, O'Connor CJ. *Colloid Polym. Sci.* 1997; **275**: 293.
- Sindorf DW, Maciel GE. *J. Am. Chem. Soc.* 1983; **105**: 3767.
- Horr TJ, Arora PS. *Coll. Surf. A: Physicochem. Eng. Asp.* 1997; **126**: 113.
- Barber M, Connor J, Guest MF, Hillier IH, Schwarz M, Stacey M. *J. Chem. Soc. Faraday Trans. II* 1973; **69**: 551.
- Kim SJ, Matsumoto M, Shigehara K. *Synth. Met.* 1999; **105**: 27.
- Ashkenasy G, Ivanisievic A, Cohen R, Felder CE, Cahen D, Elis AB, Shanzer A. *J. Am. Chem. Soc.* 2000; **122**: 1116.
- Mills P, Sullivan JL. *J. Phys. D* 1983; **16**: 723.
- Srivastava S, Badrinarayanan S, Mukhedkar AJ. *Polyhedron* 1985; **4**: 409.
- Maroney MJ, Fey EO, Baldwin DA, Stenkamp RE, Jensen LH, Rose NJ. *Inorg. Chem.* 1986; **25**: 1409.