

# X-ray photoelectron spectroscopy study of adsorption of (3-mercaptopropyl)trimethoxysilane and *n*-propyltriethoxysilane on a rutile TiO<sub>2</sub>(110) surface

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## ABSTRACT

We have studied the adsorption of two silane compounds, (3-mercaptopropyl) trimethoxysilane (MPTMS) and *n*-propyltriethoxysilane (PTES), on a rutile TiO<sub>2</sub>(110) surface using angle dependent X-ray photoelectron spectroscopy. The observation of the S 2p line, in the case of MPTMS, and the C 1s line for both MPTMS and PTES confirms the adsorption of the molecules. For a dose of 122 Langmuirs of MPTMS we find room temperature coverage of 0.55 monolayers, while for a 60 Langmuir dose of PTES the coverage is found to be 0.89 monolayers. Thus, MPTMS has a considerably lower sticking coefficient on the rutile TiO<sub>2</sub>(110) surface than PTES. Both PTES and MPTES are found to bind dissociatively to the surface. An analysis of angle dependent data further suggests that for MPTMS the thiol group and thus alkyl chain points away from the surface, while for a 0.5 monolayer coverage of PTES the alkyl chain is oriented towards the surface. A higher coverage, ~1 monolayer, the behavior seems to be reversed for at least a fraction of all molecules. Temperature programmed XPS measurements suggest that the oxy groups of both molecules desorb from the surface at 550 K, which is in accordance with literature. The present study thus provides information on how these silane coupling agents bind to titanium oxide and what their molecular orientation is on the surface. Copyright © 2015 VBRI press.

**Keywords:** (3-mercaptopropyl) trimethoxysilane; *n*-propyltriethoxysilane; silane coupling agents; titanium dioxide; XPS.



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## Introduction

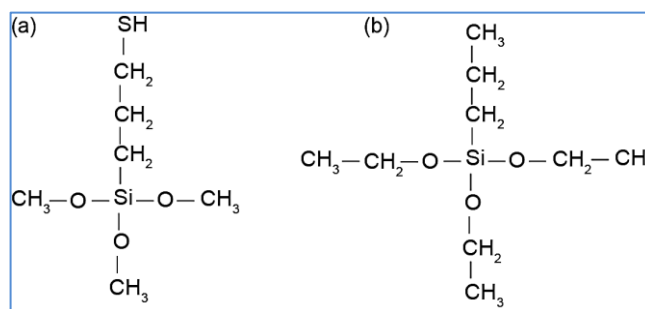
Self-assembled monolayers of organosilanes have shown their potential to alter the surface properties of metals and semiconductors to make them applicable in biomedical [1], energy efficient [2] and microelectronics devices [3]. Organosilanes have been most frequently used as coupling agents in biomedical devices for the immobilization of functional nano-objects [4, 5] and biomolecules [6] such as DNA [1], enzymes [7] and proteins [8]. Among the oxides  $\text{TiO}_2$  is one of the most intensively studied and widely used materials in, e.g., biomedical applications such as implants. The reason for its wide use is its extremely good biocompatibility, low toxicity, and high chemical stability [9, 10].

In view of the above mentioned applications we here report a study of interaction of two silanes compounds with titanium dioxide. More precisely, we have investigated the adsorption of (3-mercaptopropyl) trimethoxysilane (MPTMS) and *n*-propyltriethoxysilane (PTES) on the rutile  $\text{TiO}_2(110)$  surface (see Fig. 1 for the chemical structure of the compounds). The two compounds are chemically very similar, with MPTMS having a sulfur-terminated alkyl chain, whereas PTES contains an alkyl chain without any functional group. Here we find that MPTMS adsorbs with the thiol group pointing away from the surface, whereas PTES binds with the alkyl chain pointing towards the surface for low coverage ( $\sim 0.5$  monolayer). For higher coverage ( $\sim 1$  monolayer) we find that at least a fraction of the molecules is oriented with the alkyl chain towards the vacuum interface, i.e. away from the surface.

## Experimental

The measurements were performed at the XPS end station [11] of the SPECIES beam line of the MAX IV Laboratory in Lund, Sweden. The setup consists of a preparation chamber equipped with a sputter gun and further preparation and surface analysis tools and a separate analysis chamber equipped with a SPECS Phoibos 150-NAP hemispherical electron energy analyzer. The present data were obtained using a non-monochromatized SPECS XR 50 Mg  $K_\alpha$  x-ray anode (photon energy 1253.6 eV) operated at 12.5 kV and 20 mA emission current. At the time of the present experiments the base pressure of both chambers was in the low  $10^{-9}$  mbar range. *n*-propyltriethoxysilane (PTES,  $> 98\%$ ) and (3-mercaptopropyl) trimethoxysilane (MPTMS, 95%) were purchased from Sigma-Aldrich and rutile  $\text{TiO}_2(110)$  crystals of dimensions  $10 \times 10 \times 1 \text{ mm}^3$  from PI-Kem, England. To measure the temperature, a K-type thermocouple was attached to the sample holder in close proximity of the crystal edge. The crystal was cleaned by several cycles of argon ion sputtering for 10 min at an energy of 1 keV and subsequent annealing at  $590^\circ\text{C}$  for 15 minutes. The MPTMS and PTES molecules were degased via freeze-pump-thaw cycles and dosed through a leak valve attached to the preparation chamber at room temperature. The molecular thin films were dosed in the preparation chamber. Doses are expressed in Langmuirs ( $1 \text{ L} = 1.33 \times 10^{-6} \text{ mbar s}$ ). Investigated dose were 121 L for MPTMS and 11 L and 60 L for PTES. The spectra were

measured in normal and grazing emission geometries at emission angles of  $0^\circ$  and  $75^\circ$  with respect to the surface normal. All spectra were calibrated using the Ti 2p line, which in turn was calibrated to the Au 4f line measured on a gold foil in good ohmic contact with the  $\text{TiO}_2$  crystal. A polynomial-type background was subtracted from the Ti 2p, and S 2p spectra; for the C 1s and O 1s lines a Shirley-type background was removed. Si 2p x-ray photoelectron spectra were also measured, but not further considered here, since the  $\text{TiO}_2$  crystal contained a small, inhomogeneous contamination of silicon (on the level of less than 1% of a monolayer) obscuring the signal.



**Fig. 1.** Schematic of the here studied silane compounds: (a) (3-mercaptopropyl) trimethoxysilane, (b) *n*-propyltriethoxysilane.

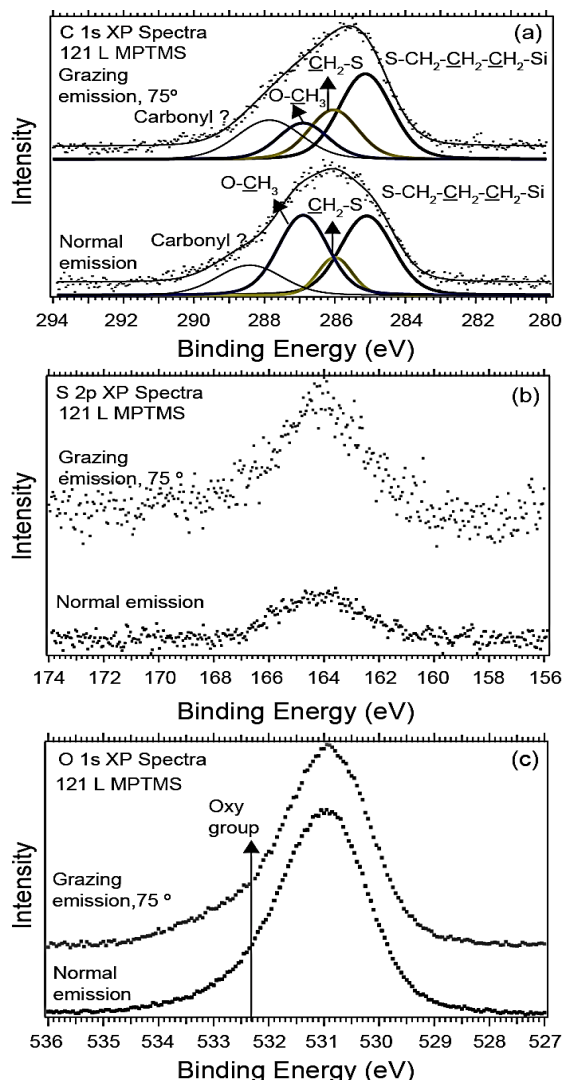
## Results and discussion

Fig. 2(a)-(c) shows the C 1s, S 2p and O 1s x-ray photoelectron (XP) spectra for a dose of 121 L of MPTMS. The C 1s line (Fig. 2(a), normal emission) can be deconvoluted into four components: a component for alkyl chain carbon atoms,  $\text{HS}-\text{CH}_2-\underline{\text{CH}_2}-\text{CH}_2-\text{Si}$ , at 285.17 eV (core-ionized atom underlined), methoxy carbon,  $\underline{\text{CH}_3}-\text{O}-\text{Si}$ , at 286.03 eV, sulfur-bonded carbon,  $\underline{\text{CH}_2}-\text{S}$ , at 286.87 eV, and a carbonyl species discussed below at 288.42 eV. The intensity ratio of the alkyl chain component to that of  $\underline{\text{CH}_2}-\text{S}$  is 2:1, which suggests the non-dissociation of the mercaptopropyl chain, whereas the low intensity of the  $\underline{\text{CH}_3}-\text{O}-\text{Si}$  component and presence of an additional peak at high binding energy indicates the dissociation of one or more MPTMS methoxy groups per molecule to form carbonyl species. The C 1s spectra measured using grazing emission show an increase in peak intensity related to the mercaptopropyl chain and a reduction in intensity of the methoxy component, which suggests that the thiol group points away from the surface, while the methoxy groups are closer to the surface. The areas of the S 2p line measured at grazing emission increases compare to normal emission further indicates about the orientations of MPTMS (Fig. 2(b)). A shoulder in the O 1s spectra at 532.2 eV (Fig. 2(c)), which is found in addition to the main component related to photoemission from the  $\text{TiO}_2$  support at 530.9 eV, is attributed to oxy groups of the MPTMS molecules.

Quantitatively, the MPTMS coverage for the 121 L dose can be calculated from a comparison of the Ti 2p intensity measured after dosing of the molecules to that of the clean surface according to

$$I_{\text{atten}} = I_0 \left[ 1 - \Theta_A + \Theta_A \exp\left(\frac{-a}{\lambda} \cos \theta\right) \right], \quad (1)$$

where  $I_{atten}$  is the attenuated intensity after adsorption of PTES,  $I_0$  the intensity measured for the clean surface,  $\theta_A$  the fractional coverage,  $a$  the size of the MPTMS molecules ( $\sim 0.9$  nm estimated from the bond lengths),  $\theta$  the emission angle of the photoelectrons, and  $\lambda$  the attenuation length of the photoelectrons. Evaluating this equation gives a MPTMS coverage of 0.55.



**Fig. 2.** XPS spectra for MPTMS/TiO<sub>2</sub>(110). (a) C 1s, (b) S 2p, and (c) O 1s lines for a dose of 121 L.

The C 1s and O 1s XP spectra for a PTES dose of 11 L are shown in **Fig. 3(a)** and **(b)**. In the O 1s spectrum in **Fig. 3(b)** a high binding energy shoulder is related to molecule adsorption, while the main component is due to photoemission from the support. The C 1s XP spectrum in **Fig. 3(a)** can be interpreted in terms of the molecular structure of PTES: the molecule contains 6 types of chemically similar carbon atoms bonded to adjacent carbon, hydrogen, and silicon atoms. These carbon atoms have approximately the same C 1s binding energy ( $\text{CH}_3\text{-CH}_2\text{-O}$ ,  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-Si}$ , at  $\sim 285.5$  eV, peak C1). In addition, PTES contains 3 carbon atoms bonded to oxygen ( $\text{CH}_3\text{-CH}_2\text{-O-Si}$ , peak C2) with a C 1s binding energy of

$\sim 286.7$  eV. Hence, the C1:C2 intensity ratio is expected to be 2:1, which is as observed in **Fig. 3(a)**. While the C 1s lineshape thus might indicate associative adsorption, it should be noted that also the carbon atoms of surface-bonded ethoxy groups are found to have the same C 1s binding energy and that a splitting-off of the ethoxy groups thus cannot be excluded. Indeed, Gamble *et al.* [12] found for tetraethyl orthosilicate (TEOS), chemically similar to PTES and MPTMS, that the molecule binds dissociatively to the TiO<sub>2</sub>(110) surface. A fraction of the molecular oxy groups are split off already below room temperature and bind to both five-fold coordinated Ti atoms as well as bridging oxygen vacancies. While the oxy groups bonded to the five-fold coordinated Ti atoms leave the surface already at room temperature as ethanol, the vacancy-bonded ethoxy groups stay at the surface at temperatures below 550 K and desorb as ethylene and ethanol by  $\beta$ -hydride elimination at higher temperature.

In addition to the C 1s double peak with the two main components discussed above, small shoulders are observed at  $\sim 288.42$  eV (for MPTMS), 288.3 eV (for PTES) and 290.2 eV (for PTES, normal emission (cf. **Fig. 3(a)**). We attribute these shoulders to the further transformation of oxy groups into a carbonyl species. It can be noted that such a reaction towards a carbonyl probably requires initial dissociation of some of the ethoxy ligands from the molecule and direct binding to the surface as described above.

In grazing emission the intermediate oxygen- and thus clearly ethoxy-related C2 component in the C 1s spectrum becomes more pronounced (cf. **Fig. 3(a)**). Since photoemission in grazing emission geometry is more surface sensitive than photoemission in normal emission geometry, this indicates that the propyl chain points towards the surface, while the ethoxy groups – or possibly the fraction of the ethoxy groups which remains bonded to the Si atom – are directed away from the surface. Similarly, the molecule-related high binding energy shoulder in the O 1s spectrum becomes pronounced in grazing emission geometry (**Fig. 3(b)**). This provides further evidence for the hypothesis that the Si-bonded ethoxy groups point away from the surface.

The spectra for a higher PTES dose of 60 L dose are shown in **Fig. 3(c)** and **(d)**. The lineshape of the C 1s line measured in normal emission resembles that measured for the 11 L dose in grazing emission. This suggests that the molecule geometry at higher coverage (0.9 monolayers) at least partially is reverse that found for low coverage (0.6 monolayers). The calculated coverage calculated from the attenuation of the Ti 2p signal (using equation (1), where the size of PTES molecule  $\sim 1.1$  nm) is 0.58 for a dose of 11 L and 0.89 for a dose of 60 L.

**Fig. 4** shows the evolution of the C 1s spectrum as a function of temperature after dosing 111 L of PTES (temperature-dependent XPS, TD-XPS). The C2 peak disappears at around 550 K, while the C1 component remains quite intact until 700 K and vanishes completely at 800 K. The relatively high desorption temperature for the ethoxy groups, of which the C2 peak is characteristic, suggests the bonding of ethoxy groups to surface



vacancies. Further the high desorption temperature for the C1 components suggest that at low coverage (less than a monolayer) the propyl chain is chemically bonded to the surface. Similar TD-XPS results were also observed for MPTMS suggesting a desorption temperature for the methoxy groups at 550 K, while a hydrocarbon species stays on the surface until 800 K.

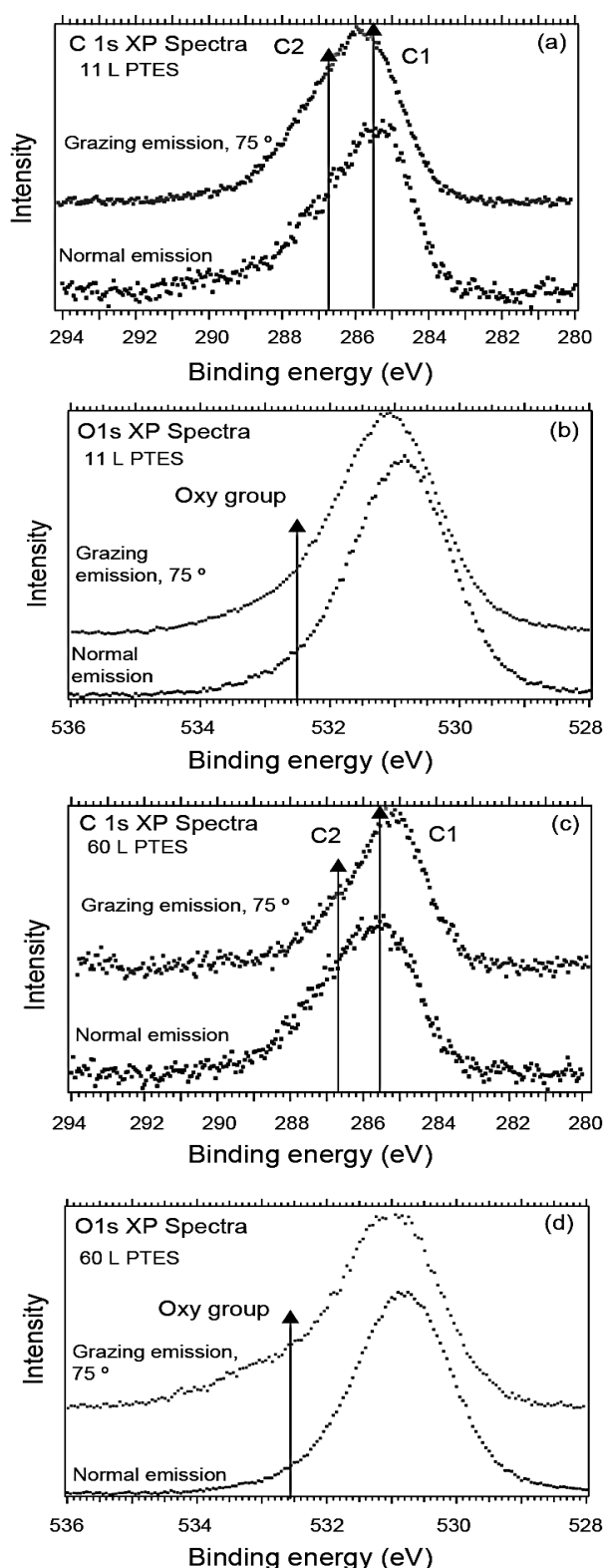


Fig. 3. XP spectra for PTES/TiO<sub>2</sub> (110). (a) C 1s, (b) O 1s spectra for 11 L dose. (c) C 1s, and (d) O 1s 2p spectra for 60 L dose.

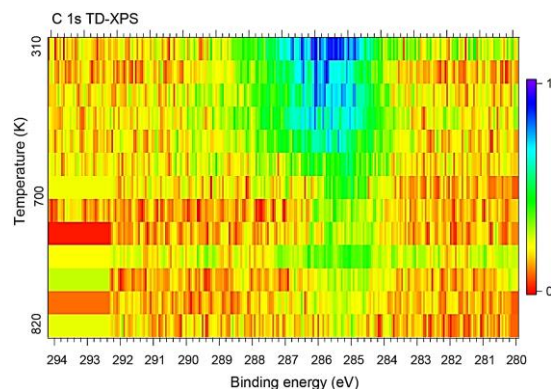


Fig. 4. C 1s TD-XPS measurements performed for a layer of PTES molecules formed from dosing 111 L. The color scale shows the intensity.

## Conclusions

In summary, we have studied the growth of MPTMS and PTES on the rutile TiO<sub>2</sub>(110) surface in a controlled fashion. The adsorption was confirmed from the observation of the core levels expected from the molecular structure of both silane molecules. The initial analysis indicates that MPTMS and PTES adsorb dissociatively. In the case of MPTMS the thiol chain points away from the surface. The form of the C 1s line shape observed for low coverage (~0.5 monolayers) of PTES indicates that the long alkyl chain points towards the surface, whereas it, at least for a fraction of the adsorbates, points away from the surface for higher coverage (~1 monolayer). The comparison of the coverage for a dose of 121 L of MPTMS to a 60 L dose of PTES indicates a lower sticking coefficient for MPTMS molecules on rutile TiO<sub>2</sub>(110) as compared to PTES. TD-XPS suggests desorption of the methoxy/ethoxy groups at 550 K, which might be chemically bonded to surface bridging oxygen vacancies. A hydrocarbon residue desorbs at 800 K.

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