

# Spectroscopic characterisation of self-assembled monolayers of alkylsiloxanes on SrTiO<sub>3</sub>

Boike L. Kropman, Dave H.A. Blank, Horst Rogalla

*University of Twente, Dept. of Applied Physics, P.O. Box 217, 7500 AE Enschede, The Netherlands*

Received 26 September 1996

## Abstract

Self-assembled monolayers of alkyltrichlorosilanes have been successfully prepared on SrTiO<sub>3</sub> substrates. Characterisation has been performed by atomic force microscopy (AFM), wettability, ellipsometry, angle resolved X-ray photoemission spectroscopy (ARXPS) and reflection absorption infrared spectroscopy (RAIRS). It is found that dense and ordered monolayers form if environmental conditions are controlled. Good agreement is found for the ellipsometry thickness and the ARXPS thickness. From simulations of absorption spectra, we find that the molecules are oriented with an average tilt angle of  $-11^\circ$  with respect to the surface normal on the (001) and (110) faces. On the niobium-doped SrTiO<sub>3</sub> substrate, however, the tilt angle increases to  $-35^\circ$ . © 1998 Elsevier Science S.A.

*Keywords:* Alkyltrichlorosilanes; Ellipsometry; Monolayers

## 1. Introduction

Thin films of organic molecules have attracted a lot of attention during the past few years [1]. One way to form an ordered thin film comprised of organic molecules is by means of the self-assembly (SA) technique. This technique relies on the spontaneous adsorption of organic molecules onto a surface via a strong affinity of one of the tail groups of the molecule with the substrate (e.g. the thiol-moiety on gold), which ensures bonding of the molecule to the substrate. The chains organise themselves in an ordered fashion by minimising the van der Waals interaction between neighbouring chains. In this way stable, crystalline-like packing of molecules can be obtained, which have been studied thoroughly as model systems for intermolecular interactions, wetting, corrosion, etc.

Cubic perovskites with the ABO<sub>3</sub> structure belong to a group of oxidic crystals with a surprising number of properties. They may conduct ions, display colossal magnetoresistance and superconductivity and can exhibit magnetic properties as ferro- and antiferromagnetism. SrTiO<sub>3</sub> (STO) is a preferable substrate for thin films of these complex oxides.

We have selected SrTiO<sub>3</sub> as a model substrate for the deposition of organic monolayers via a siloxane bonding scheme [1,2]. SrTiO<sub>3</sub> is readily available in different orientations with different lattice parameters and can be made

(semi)conducting by doping with niobium. In this report, we will focus on the (spectroscopic) characterisation of simple alkyltrichlorosilanes on SrTiO<sub>3</sub>. In particular, emphasis is put on the quantitative interpretation of angle resolved XPS (ARXPS) and infrared spectroscopy (RAIRS).

## 2. Results and discussion

### 2.1. General

Prior to adsorption of the alkyltrichlorosilane, the SrTiO<sub>3</sub> substrates<sup>1</sup> were sonicated in a sequence of solvents (chloroform, acetone and ethanol) several times, followed by a short (1 min) dip in dilute phosphoric acid. For each adsorption, the solution was freshly prepared by dissolving  $\sim 1$  mM octadecyltrichlorosilane (OTS) in n-hexadecane (HD). The temperature and relative humidity during deposition were controlled as well as possible, i.e. the adsorption took place in a desiccator to minimise the influence of environmental humidity (relative humidity during adsorption was 20–40%) and the temperature was controlled at 20°C. Adsorption times were kept between 2 and 12 h, although no difference in film quality was found for these extremes. To remove physisorbed

<sup>1</sup> SrTiO<sub>3</sub> substrates were obtained from Single Crystal Technology Escete, Enschede, The Netherlands, and have different surface orientations: (001), (110), (103) and (001)-Nb-doped.

Table 1  
Results of peak fitting for high resolution XPS measurements <sup>a,b</sup>

Sample <sup>b</sup>	Si 2p	Sr 3d 5/2	Sr 3d 3/2	C 1s	Ti 2p 3/2	Ti 2p 1/2	O 1s <sup>c</sup>	O 1s <sup>c</sup>
Ref. STO(001)		132.5 (0.9)	134.3 (0.9)	285.0 (1.8)	459.0 (1.0)	464.7 (1.1)	530.0 (0.8)	531.4 (2.2)
OTS/STO(001)	102.5 (1.3)	132.5 (0.9)	134.2 (1.0)	285.0 (1.2)	459.0 (1.1)	464.7 (1.2)	530.2 (0.8)	531.8 (2.4)
OTS/STO:Nb(001)	102.6 (1.4)			285.0 (1.2)	459.2 (1.2)	464.7 (1.9)	530.2 (0.8)	531.7 (2.5)
DTS/STO(001)	102.5 (1.3)	134.2 (1.0)	132.4 (1.0)	285.0 (1.3)	459.0 (1.1)	464.6 (1.4)	530.1 (0.8)	531.4 (2.2)

<sup>a</sup> Referenced to C 1s at 285.0 eV, full width at half maximum of fits are indicated between parentheses.

<sup>b</sup> DTS, dodecyltrichlorosilane.

<sup>c</sup> O 1s is fitted as two singlets.

and/or complexed HD, the monolayer was sonicated for several minutes in chloroform and ethanol.

Immediately after adsorption, the quality of the monolayer was measured by ellipsometry, wettability and atomic force microscopy (AFM). The measured thickness (using an isotropic refractive index of 1.50) of a high quality OTS monolayer was approximately 2.4 nm, which is consistent with the presence of a slightly tilted single molecular layer. The contact angles obtained also indicate the formation of a highly hydrophobic surface, consistent with a methyl-terminated surface ( $\theta_{adv}^{H_2O} > 110^\circ$ ). However, if the humidity is too high, the molecules will already polymerise in the solution, resulting in the formation of bilayers on top of the Self-Assembled Monolayer (SAM). The presence of these extra bilayers is evidenced by ellipsometry and AFM [2].

## 2.2. ARXPS

ARXPS was performed on a Kratos XSAM 800 spectrometer, using Mg X-rays ( $K_\alpha = 1254.6$  eV). Pass energies used for survey scans were 50 eV, whereas for the high resolution scans 20 eV were used. The spectra were background subtracted and fitted by a home-built computer program. All fits were made with 100% Gaussians. To determine the thickness of the monomolecular film, spectra were not only taken at zero take-off angle  $\varphi$ , but also at other angles (10, 20, 30, and 50° away from the surface normal).

Elemental analysis was done using the survey scans. Subsequently high resolution scans were made to determine the respective binding energies, see Table 1. On as-cleaned substrates only the expected elements (Sr, Ti and O) appear plus a broad carbon contamination peak. If a substrate has been derivatised with OTS, a different carbon peak and a silicon peak appear. The sharper carbon peak replaces the broad and weak contamination peak and is due to the aliphatic alkyl chain. The binding energy (BE) of the Si 2p peak, 102.5 eV, indicates the formation of a  $Si_2O_3$ -siloxane network, formed by crosslinking of neighbouring chains. The low BE oxygen peak (at  $\sim 530.1$  eV) can be assigned to the titanate oxygen, whereas the high BE oxygen peak (located at  $\sim 531.4$  eV) is due to the surface hydroxide oxygen. Upon adsorption of a SAM, the titanate oxygen peak decreases in intensity, whereas the high BE peak is shifted to a higher BE by  $\sim 0.4$

eV. The latter peak is now, at least partly, due to the siloxane oxygen. No chlorine from the alkyltrichlorosilane is present.

Angular resolved XPS shows that the hydroxyl oxygen on the as-cleaned substrate increases in intensity compared to the titanate oxygen if the take-off angle is increased (see Fig. 1). Furthermore, the siloxane oxygen is located just above the interface between the SAM and the substrate. The  $\varphi$ -dependent attenuation of photoelectrons from a specific peak in a uniform overlayer can be used to estimate the thickness of the overlayer [2,3]. We have used photoelectrons of the Sr 3d peak resulting in thicknesses for good quality films of 2.2–2.5 nm, which agrees well with the ellipsometry values. However, if we use the Ti 2p photoelectrons, we find

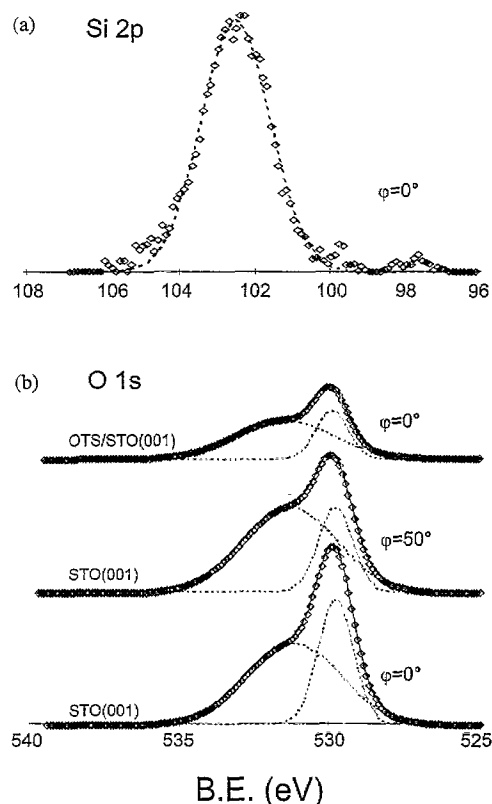


Fig. 1. High resolution spectra of (a) the Si 2p region for a monolayer of OTS on  $SrTiO_3(001)$  and (b) the O 1s region at  $\varphi=0$  and  $\varphi=50^\circ$  of an unmodified  $SrTiO_3(001)$  substrate and of alkylsiloxane SAM on  $SrTiO_3(001)$  at  $\varphi=0^\circ$ .

much thinner (1.3–1.9 nm) values. This is not yet fully understood, but the position of the  $\text{TiO}_2$  plane in the  $\text{SrTiO}_3$  lattice might play an important role.

### 2.3. RAIRS

Reflection absorption infrared spectroscopy was performed on a BioRad FTS-60A spectrometer. Infrared light ( $500\text{--}4000\text{ cm}^{-1}$ ) was reflected at variable angles of incidence at the substrate and detected by a HgCdTe detector. Between 500 and 1000 scans were co-added and averaged to obtain a good signal-to-noise ratio.

In Fig. 2, an example of a RAIRS spectrum in the C–H stretching region is shown for a monolayer of OTS on a  $\text{SrTiO}_3(001)$  substrate. Comparable spectra are obtained from substrates with a different orientation, but from the Nb-doped  $\text{SrTiO}_3$  substrate only small negative peaks are observed (not shown). The spectrum is taken at an angle of incidence  $\theta_{\text{in}}$  of  $86^\circ$ , using *p*-polarised light. Clearly visible are three peaks located at  $2849$ ,  $2918$  and  $2956\text{ cm}^{-1}$ , which are assigned, respectively, to the symmetric  $\text{CH}_2$  stretch ( $\nu_s(\text{CH}_2)$ ), the asymmetric  $\text{CH}_2$  stretch ( $\nu_a(\text{CH}_2)$ ), and the asymmetric  $\text{CH}_3$  stretch ( $\nu_a(\text{CH}_3)$ ) vibrations [4,5]. The peak positions of the methylene stretches indicate a crystal-line-like packing of the alkyl chains. Apparently, some of the specific methyl stretchings (the symmetric  $\text{CH}_3$  stretch ( $\nu_s(\text{CH}_3, \text{FR})$ ) at  $\sim 2878\text{ cm}^{-1}$ , and the out-of-plane asymmetric methyl stretch ( $\nu_a(\text{CH}_3, \text{op})$ ) at  $\sim 2965\text{ cm}^{-1}$ ) that can be observed for thiols on gold are absent [6]. In the following we will show that the absence is not due to the lack of order in the chain terminus, but that it is caused by optical effects.

It is well known that metals (e.g. gold) possess a surface selection rule that inhibits the presence of electrical field components parallel to the surface of the substrate, i.e. only components perpendicular to the surface are present. Therefore, vibrations with a dipole moment parallel to the surface are not probed by RAIRS. Non-metallic substrates (insulators, semiconductors) do not have this surface selection rule, and on these substrates parallel components will also be present in the spectra. Approximate absorption strengths of vibrational modes can be calculated by implementing the equations from Ref. [7], and subsequently these can be used to obtain a structural model of the SAMs on  $\text{SrTiO}_3$ . In Fig. 3 absorption strengths (intensities) for a virtual absorption ( $\nu = 3000\text{ cm}^{-1}$ ,  $n = 1.50$  and  $k_{\text{iso}} = 0.10$ ) on  $\text{SrTiO}_3$  ( $n = 2.209$  [8]), probed with *p*-polarised light, are shown in the case of parallel ( $A_{p\parallel}$ ) or perpendicular ( $A_{p\perp}$ ) orientation of its vibrational dipole moment. To account for anisotropy, we assume that the dipole moments are distributed uniaxially symmetric and therefore  $k_x = k_y = 3k_{\text{iso}}/2$  and  $k_z = 3k_{\text{iso}}$  [9]. For this substrate (and also  $\text{SiO}_2$  [9]),  $A_{p\parallel}$  and  $A_{p\perp}$  are always opposite in sign, and reverse sign at Brewster's angle of the substrate ( $\theta_{\text{B}} \sim 66^\circ$ ). Furthermore, the signal-to-noise ratio  $SN$  is the product of the intensity of absorption  $A$  and the reflectivity of the substrate  $R_0$ ,  $SN = A \times R_0$ . This equation yields an opti-

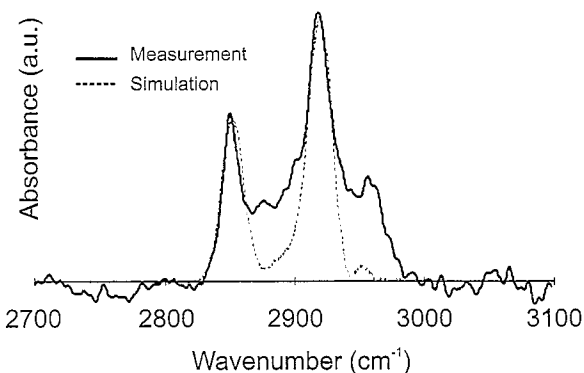


Fig. 2. Experimental (solid line) and simulated (dotted line) RAIRS spectrum of the C–H stretching region. Angle of incidence in the experiment was  $86 \pm 3^\circ$ ; the best fit was made for  $\theta_{\text{in}} = 88.8^\circ$  and  $\alpha = -11^\circ$ .

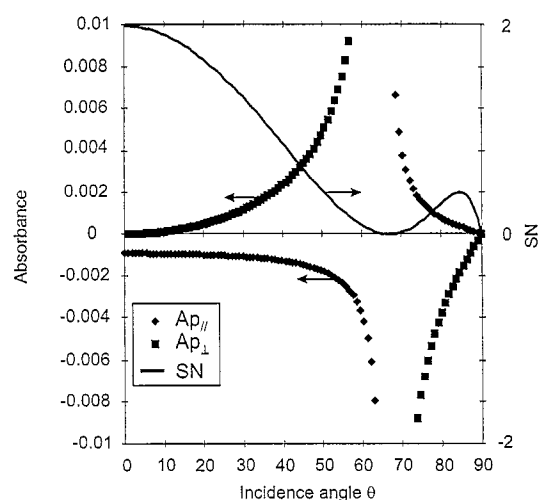


Fig. 3. Calculated absorption strength for a virtual absorption at  $\nu = 3000\text{ cm}^{-1}$ , and an isotropic absorption strength  $k_{\text{iso}} = 0.10$  ( $n = 1.50$ ), for parallel ( $A_{p\parallel}$ ) and perpendicular ( $A_{p\perp}$ ) orientation of the transition dipole moment and signal-to-noise ratio  $SN$  as a function of the angle of incidence  $\theta_{\text{in}}$ .

imum  $\theta_{\text{in}}$  for *p*-polarised light on  $\text{SrTiO}_3$  of  $0^\circ$ , and a suboptimum at  $\sim 85^\circ$  (see Fig. 3).

The molecule itself can be characterised by three angles,  $\alpha$  (tilt),  $\beta$  (azimuth), and  $\gamma$  (twist) with respect to the plane of incidence. In the case of an anisotropic film, all molecules can be assumed to have the same average orientation. Every vibration then possesses a certain tilt angle with respect to the incoming beam. The sum  $A_p$  of  $A_{p\parallel}$  and  $A_{p\perp}$  determines the total absorption strength and depends on this angle;  $A_p$  can be either positive or negative. If we consider the case for our virtual absorption, it can be seen that the absorption of a vibration with parallel dipole moment is negative, but changes sign at a tilt angle  $\alpha$  of  $52^\circ$ . The result for the complete C–H stretching region is a complex envelope function, composed of positive and negative absorption bands, depending on the orientation of the molecules.

By assuming an average orientation for the molecules, calculating the absorption intensities of the distinct absorption bands using the approximate equations from Ref. [7] and comparing the obtained spectra with the measured spec-

tra, a fit can be obtained. However, only an average tilt angle can be extracted from such fits;  $\beta$  and  $\gamma$  are not taken into account.

For OTS on  $\text{SrTiO}_3(001)$  and  $\text{SrTiO}_3(110)$ , an average tilt angle of  $-11^\circ$  is found, with an angle of incidence of  $88.8^\circ$ . The results obtained from the Nb-doped substrate are different: although there might be a difference in optical constants for the Nb-doped and the undoped  $\text{SrTiO}_3$  crystal, the difference cannot explain the observed difference in RAIRS spectra. From the other characterisation techniques that we have employed, it can be concluded that the quality of the SAMs is only slightly lower. Therefore, the only conclusion can be that the orientation of the molecules is different. From the simulations of the RAIRS spectra, one can determine that both methylene peaks decrease enormously and even become negative if  $\alpha$  is increased above  $25^\circ$ . The approximate tilt angle for an OTS monolayer on Nb-doped  $\text{SrTiO}_3$  is found to be  $-35^\circ$ .

### 3. Conclusion

We have studied the formation of alkylsiloxane monolayers on different faces of  $\text{SrTiO}_3$  substrates. The resulting films are characterised by AFM, wettability, ellipsometry,

(AR)XPS and RAIRS. Highly ordered and densely packed monolayers are formed on all substrates if the temperature and humidity during deposition are controlled below  $20^\circ\text{C}$  and 40%. Above these values, thicker layers form by means of bilayers absorbed onto the single molecular layer. Simulation of the RAIRS spectra yields an average molecular orientation on  $\text{SrTiO}_3(001)$  and  $(110)$  substrates with small tilt angles ( $\alpha = -11^\circ$ ), whereas on the Nb-doped substrate a larger average tilt angle is found ( $\alpha \sim -35^\circ$ ).

### References

- [1] A. Ulman, *An Introduction to Ultrathin Organic Films*, from Langmuir-Blodgett to Self-Assembly, Academic, San Diego, CA, 1991.
- [2] B.L. Kropman, D.H.A. Blank, H. Rogalla, *Supramol. Sci.* 4 (1997) 59–65.
- [3] W.A.M. Aamink, A. Weishaupt, A. van Silfhout, *Appl. Surf. Sci.* 45 (1990) 37.
- [4] R.G. Snyder, *Macromolecules* 23 (1990) 2081.
- [5] D.L. Allara, R.G. Nuzzo, *Langmuir* 1 (1985) 52.
- [6] M.D. Porter, T.B. Bright, D.L. Allara, C.E.D. Chidsey, *J. Am. Chem. Soc.* 109 (1987) 3559.
- [7] J.A. Mielczarski, R.H. Yoon, *J. Phys. Chem.* 93 (1989) 2034.
- [8] E.D. Palik (Ed.), *Handbook of Optical Constants of Solids*, Academic, Orlando, FL, 1985.
- [9] H. Hoffmann, U. Mayer, A. Krischanitz, *Langmuir* 11 (1995) 1304.