Supporting Information

Interface Chemistry and Molecular Bonding of Functional Ethoxysilane-Based Self-Assembled Monolayers on Magnesium Surfaces

Manuela S. Killian,[†] Steffen Seiler,[‡] Victoria Wagener,[†] Robert Hahn,[†] Christina Ebensperger,[‡] Bernd Meyer,[‡] Patrik Schmuki^{†,¶,*}

[†]Department of Materials Science and Engineering, Chair for Surface Science and Corrosion, Friedrich-Alexander-University Erlangen-Nürnberg, Martensstr. 7, 91058 Erlangen, Germany

[‡]Interdisciplinary Center for Molecular Materials (ICMM) and Computer-Chemistry-Center (CCC), Friedrich-Alexander-University Erlangen-Nürnberg, Nägelsbachstr. 25, 91052 Erlangen, Germany

[¶]Department of Chemistry, King Abdulaziz University, Jeddah, Saudi Arabia

*Email: schmuki@ww.uni-erlangen.de

XPS - O1s signal



Figure S1. a) O1s signal of a thick APTES layer, an APTES SAM on Mg(OH)₂ and the pure Mg(OH)₂ surface. b) Fit of the APTES SAM O1s signal.

The O1s signal recorded for the SAM (531.7 eV) is shifted to lower binding energies compared to a thick layer of APTES (532.3 eV), but still showing a higher binding energy value than the pure oxide (531.4 eV). This shift can be caused by either an overlap of the APTES and oxide signal or by a transformation of Si $-O-C_2H_5$ to Si-O-Mg or Si-O-Si, i.e., covalent adsorption or cross-linking. Therefore, the APTES SAM O1s region was fitted for the oxide and molecule contribution. The oxide signal was fitted with the parameters obtained from the pure oxide sample and the area was calculated from the Mg at%–value. A binding energy of 531.8 eV was determined for the SAM O1s signal, indicating chemical bond formation. In Ref. [16] the XPS signals were charge-corrected to Mg 2p (50.2 eV), leading a binding energy of 400 eV for N1s. When the same reference signal is chosen (Mg 2p or C1s respectively), the N1s signal of Ref. [16] shows identical binding energy values to the here reported signal.

Assignment of the ToF-SIMS signals

	m/z	assignment
Fig 2a	m/z=23.99	Mg ⁺
Fig 2b	m/z=30.03	$\rm CH_4N^+$
Fig 2c	m/z=43.96	SiO^+
Fig 2c	m/z=44.00	$\rm SiH_2N^+$
Fig 2c	m/z=44.05	$\rm C_2H_6N^+$
Fig 2d	m/z=57.98	$\rm SiCH_2O^+$
$\operatorname{Fig} 2d$	m/z = 58.01	$\rm SiCH_4N^+$
$\operatorname{Fig} 2d$	m/z = 58.03	$\rm C_2H_4NO^+$
$\operatorname{Fig} 2d$	m/z = 58.07	$\rm C_3H_8N^+$
Fig 2e	m/z=67.96	Si-O-Mg ⁺
Fig 2e	m/z=68.00	$\rm SiC_2H_2N^+$
Fig 2e	m/z=68.05	$\rm C_4H_6N^+$
Fig 2e	m/z=68.06	$C_5H_8^+$
$\operatorname{Fig} 2 \mathrm{f}$	m/z = 71.95	$\rm Si-O-Si^+$
$\operatorname{Fig} 2f$	m/z = 71.97	$\rm SiH_2N_2^+$
$\operatorname{Fig} 2f$	m/z = 71.99	$\rm SiCH_2NO^+$
$\operatorname{Fig} 2f$	m/z = 72.03	$\rm SiC_2H_6N^+$
$\operatorname{Fig} 2 \mathrm{f}$	m/z = 72.05	$\rm C_3H_6NO^+$
$\operatorname{Fig} 2f$	m/z = 72.08	$\rm C_4H_{10}N^+$
$\operatorname{Fig}2\operatorname{g}$	m/z = 191.93	${\rm Si}_4{\rm O}_5^-$
$\operatorname{Fig}2\operatorname{g}$	m/z = 192.12	$\mathrm{C_{7}H_{18}NO_{3}Si^{-}}$
$\operatorname{Fig}2\mathrm{h}$	m/z = 219.91	$\mathrm{Si}_5\mathrm{O}_5^-$
Fig 2h	m/z=220.15	$\mathrm{C_9H_{22}NO_3Si^-}$
Fig 2i	m/z = 255.23	$\mathrm{C_6H_{19}N_2O_5Si_2^-}$

Table S1. Assignment of fragments in Fig. 2 according to exact mass and isotopic pattern. Signals were assigned according to the ToF-SIMS 5 database.

Desorption of contaminants



Figure S2. Desorption of contaminants during the heat treatment in UHV.

Phthalate $(m/z=149.02 - C_8H_3O_5^+)$ and carbohydrate contaminations $(m/z=55.06 - C_4H_7^+)$ are desorbing during heating of the sample.

 $\begin{array}{ll} {\rm Residual\ signals\ in\ spectra:} & m/z{=}148.91-{\rm Si_{3}HO_{4}^{+}},\\ & m/z{=}54.98-{\rm SiCHN^{+}},\\ & m/z{=}55.00-{\rm SiC_{2}H_{3}^{+}},\\ & m/z{=}55.02-{\rm C_{3}H_{3}O^{+}},\\ & m/z{=}55.04-{\rm C_{3}H_{5}N^{+}}. \end{array}$