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An anchoring strategy for photoswitchable biosensor technology: azobenzene-modified SAMs on Si(111)

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Abstract A mild and efficient procedure has been developed to obtain covalently attached self-assembled monolayers (SAMs) on Si(111) with photochromic azobenzene head-groups. Starting from neat or diluted carboxylic acid functionalized monolayers on-chip coupling reactions were applied to attach hydroxyl-functionalized azobenzene units to the SAMs by ester bond formation. The modified surfaces were characterized by high-resolution X-ray photoelectron spectroscopy (XPS), transmission Fourier transform infrared spectroscopy (FT-IR), and contact angle measurements. Reversible *cis* ↔ *trans* isomerizations of photoswitchable SAMs were monitored by wettability measurements.

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1 Introduction

Customized and well-defined surface structures on the nanometer scale are the foundation of future technological applications. A promising approach to design such interfaces is using the concept of self-assembly of organic molecules on inorganic, metal, and semiconductor surfaces. Self-assembled monolayers (SAMs) possess an enormous potential in the fields of molecular electronics and biological sensing devices [1–4]. Covalently bound monolayers on semiconductors enable the incorporation of chemical and biological functionalities into solid state devices, e.g., chemosensors or biosensors. Silicon, as one of the most widely used materials, opens the opportunity to take advantage of established processing and fabrication techniques from microelectronics and semiconductor industries. Especially alkyl SAMs on crystalline silicon covalently bound to the oxide free surface provide highly stable, densely packed, and very robust systems, which are passivated and therefore stable against oxidation and other side reactions occurring in a biological environment [5–7]. Using this approach different biologically relevant molecules, such as amino acids, proteins, and DNA strands, were already covalently bound to functionalized monolayers on silicon [8–17]. A key step for anchoring defined structures is the development of a sophisticated surface chemistry. High coverage of the respective molecules is required for a sensor with high resolution. An ideal bio-sensing device must possess an extremely homogeneous surface with tailor-made chemical properties and functionalities, e.g., for selective binding of a protein, while rejecting all other possible binding partners.

Dedicated with respect and compliments to Professor Helmut Schwarz on the occasion of his 65th birthday.

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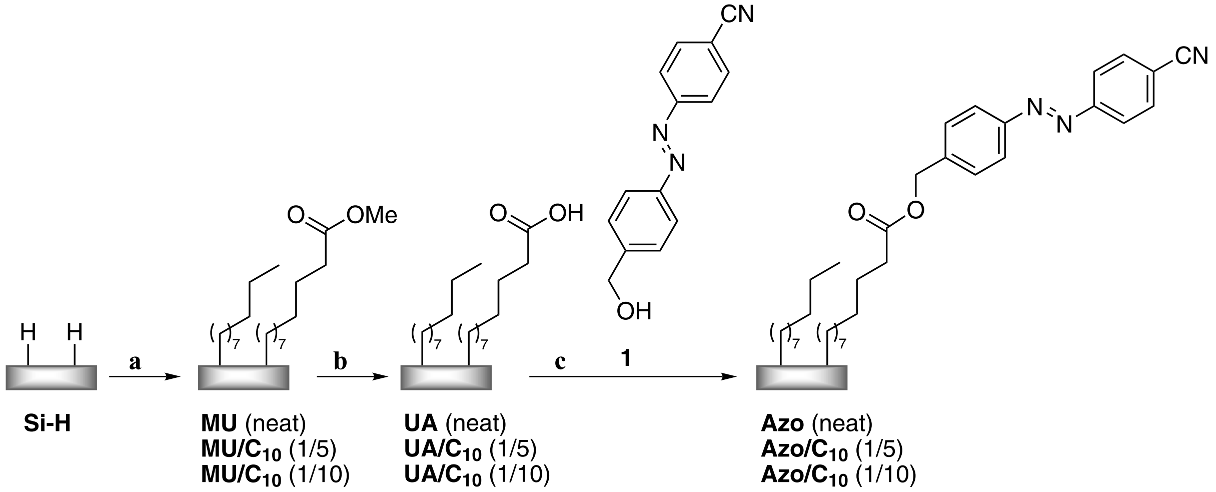

Fig. 1 Preparation of azobenzene-terminated alkyl monolayers bound to Si(111). Reagents and conditions: (**a**) Methyl 10-undecenoate (**MU**, neat) or mixtures of **MU** and 1-decene (**C_{10}**) (0.2 M in mesitylene), 160°C, 20 h; (**b**) 2 M HCl, 70°C, 2 h; (**c**) 0.01 M **1**, 0.01 M HCTU, 0.01 M DIEA, MeCN/DMF, rt, 2 h

By combining the concept of self-assembly with the unique features of photoswitchable compounds new fields and possibilities for tailor-made light-sensitive nanostructures on surfaces are opened [18]. Azobenzenes among other photoswitches[1] have been studied extensively over the last decades. The exceptional photochemical characteristics of this class of photochromic compounds are based on the two N=N double bond isomers. The thermodynamically stable *trans*-isomer changes to the *cis*-isomer in the presence of UV light and is recovered by thermal relaxation or visible light irradiation [22]. Azobenzene molecules were incorporated successfully into different self-assembled monolayers on gold and silicon and were used to reversibly manipulate different surface properties (wettability, polarity, reflectivity) by illumination with UV light [23–27]. A promising approach toward the control of cell adhesion could already be achieved on PMMA by coating with an azobenzene-based spacer containing cell adhesive binding sites as head groups [28].

Herein we report the on-chip modification of pre-assembled ω-substituted carboxylic acid monolayers on Si(111) with functionalized azobenzene molecules **1** resulting in photo-controllable SAMs, as illustrated in Fig. 1. Furthermore mixed monolayers were synthesized by dilution of the ω-functionalized precursors with inert *n*-alkyl chains enabling a well defined surface density of photoswitchable azobenzene moieties (Fig. 1).

Azobenzene compound **1** was chosen in order to obtain photosensitive SAMs with nitrile end-groups which can be chemically transformed into other functionalities, e.g., hydroxymethylene, aminomethylene or carboxylic acid groups, allowing the attachment of biomolecules by covalent or hydrogen bonds. Furthermore, the C≡N head-group can be used as an antenna to discriminate between the two isomeric states, *cis* and *trans*, of azobenzene **1** on the silicon surface by characterization techniques as, e.g., FT-IR and near-edge X-ray absorption fine structure (NEXAFS) measurements.

2 Experimental

2.1 General information

1-Decene (**C_{10}**, 94%), 10-undecylenic acid (**UA**, 98%), methyl 10-undecenoate (**MU**, 96%), mesitylene (98%), *N*,*N*-diisopropylethylamine (98%, DIEA), 1*H*-benzotriazolium 1-[*bis*(dimethylamino)methylene]-5-chlorohexafluorophosphate (1-),3-oxide (HCTU, 99.7%), acetonitrile (HPLC grade), and *N*,*N*-dimethylformamide (DMF, p.a.) were purchased and used as received, unless otherwise noted. Acetone, chloroform, hexane, methanol, and dichloromethane were spectroscopic grade (Alfa Aesar). 4-{[4-(hydroxymethyl)phenyl]diazenyl} benzonitrile **(1)** was synthesized from (4-aminophenyl)methanol and 4-nitrosobenzonitrile by following the procedures described in [29]. All 1-alkenes were distilled under reduced pressure prior to use and stored under argon at −10°C. Mesitylene (98%) was freshly distilled from sodium under nitrogen at ambient pressure. All cleaning reagents (30% H_2O_2, 96% H_2SO_4) and etching reagents (40% NH_4F) were of VLSI grade (Puranal, Riedel de Haen). MilliQ water (18.2 MΩ cm, from a MilliPore four bowl system) was used for rinsing the samples. The silicon substrates used were pieces (approximately 1 × 1 cm^2)

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[1] For other classes of photochromic compounds see [19–21].

of phosphorus (7.5 Ω cm) doped one-side polished silicon(111) wafers (Silchem, Germany). The synthesis of compound **1** and **2** is described in detail in the electronic supplementary material (ESM).

2.2 Monolayer preparation

To remove physisorbed organic material pieces of single-side polished silicon(111) were cleaned by sonication in hexane, chloroform, and methanol followed by drying under a stream of nitrogen. Afterwards they were oxidized in a freshly prepared "piranha" solution (H_2SO_4/H_2O_2 4:1, v/v) by heating to 100°C for 30 min, followed by copious rinsing with MilliQ water. **CAUTION:** "*piranha*" *solution reacts violently with organic materials and must be handled with extreme care*. The oxidized wafers were etched with deoxygenated NH_4F (40% aqueous solution) for 10 min to remove native oxide and to obtain hydrogen-terminated silicon (Si–H) [30]. The freshly prepared H–Si(111) samples were transferred into Schlenk tubes containing a deoxygenated solution of methyl 10-undecenoate (**MU**) or mixtures of **MU** and 1-decene (**C**$_{10}$) in mesitylene (4–6 mL, 0.2 M) and heated to 160°C for 20 h under an inert gas atmosphere. After the reactions were completed the samples were washed several times with hexane and dichloromethane and dried under argon. By using this method the following samples were obtained **MU**(neat), **MU/C**$_{10}$(1/5), and **MU/C**$_{10}$(1/10).

2.3 Monolayer modification

Cleavage reactions of ester-terminated monolayers for obtaining the corresponding carboxylic acid-terminated SAMs were done with 2 M aqueous HCl (10 mL) at 70°C for 2 h followed by copious rinsing with MilliQ water yielding **UA**(neat), **UA/C**$_{10}$(1/5), and **UA/C**$_{10}$(1/10) samples [8]. Esterification reactions of the carboxylic acid-terminated monolayers with the azobenzene building block **1** on the surface were realized by immersion of the samples into a 0.01 M solution of HCTU (1 equiv), DIEA (1 equiv) and 4-{[4-(hydroxymethyl)phenyl]diazenyl}benzonitrile **(1)** (1 equiv) in acetonitrile/DMF (10/1 mL) for 2 h at room temperature followed by rinsing with appropriate organic solvents furnishing **Azo**(neat), **Azo/C**$_{10}$(1/5), and **Azo/C**$_{10}$ (1/10) SAMs.

2.4 Surface characterization

Contact angle measurements were performed on a commercially available instrument (Easydrop, Krüss, Germany) using the sessile drop method. All measurements were done at ambient temperature and humidity. Each sample was prepared in triplicate at least. Usually 5 or more drops of MilliQ water with a volume of 1 µL were placed on each sample and measured. The typical average error was ±2° at maximum. Measurements of the irradiated silicon samples were done in the dark. The light source of the goniometer was covered with a red acryl filter to cut off the wavelength range between 200 and 600 nm to avoid *cis*↔*trans* isomerizations during the measurements.

The X-ray photoelectron spectroscopy (XPS) measurements were performed at beamline U41/1-PGM at BESSY II. The energy resolution of the light source was $E/\Delta E = 4800$. The horizontally polarized beam hit the surface under a grazing incidence angle of 15° and emitted electrons were detected along the surface normal. Beam damage of the organic molecules was reduced by cooling the samples to 90 K. In addition the sample was moved out of focus of the X-ray beam. For further details of the experimental setup we refer to the article by Schmidt et al. in the current issue. The analyzer resolution was better than 0.2 eV as derived from the width of the Fermi level of a clean gold sample. The XPS spectra were decomposed into least square fits of Voigt profiles with a fixed Lorentzian width and a Shirley background [31]. The intensities of the C 1s, N 1s, and O 1s core level spectra were normalized to the overall intensity both of the clean Si 2p doublet and those that are oxygen shifted. All XPS spectra have been referenced to the Si $2p_{3/2}$ level at a binding energy of 99.42 eV. Generally, this procedure allows us to correct for differential shifts caused by band bending, i.e., the concomitant surface photovoltage. However, if nanoscale islands of silicon oxide and functionalized surface coexist, averaging over both may induce photovoltage shifts of the Si 2p core level not representative for the functionalized surface.

FT-IR spectra from the modified silicon samples were collected in the transmission mode with the single point detector in the Perkin–Elmer "Spotlight" system. Air or clean oxidized silicon samples were used to generate background spectra for subtraction and/or taking ratios. The samples were slightly tilted when placed on the sample stage to minimize interference fringes. Spectra were acquired with an aperture size of 1000 × 1000 µm; a total of 1024 scans with 4 cm^{-1} resolution were averaged for each spectrum.

2.5 Irradiation experiments

Photoirradiation was performed using a high-pressure mercury lamp 200 HBO (Osram, Munich) with a 340 ± 2 nm interference filter (Amko, Tornesch). The illumination power of 1.8 $\mu W/cm^2$ at 340 nm was measured with a photometer IL-1400 (International Light). Silicon samples were placed under an inert gas atmosphere in a $1 \times 1 \times 4\ cm^3$ quartz cuvette at the focus of the irradiation beam (suprasil lens, focus 10 cm) and 2 cm behind the filter and were illuminated for 10 minutes. All experiments were done with an IR filter

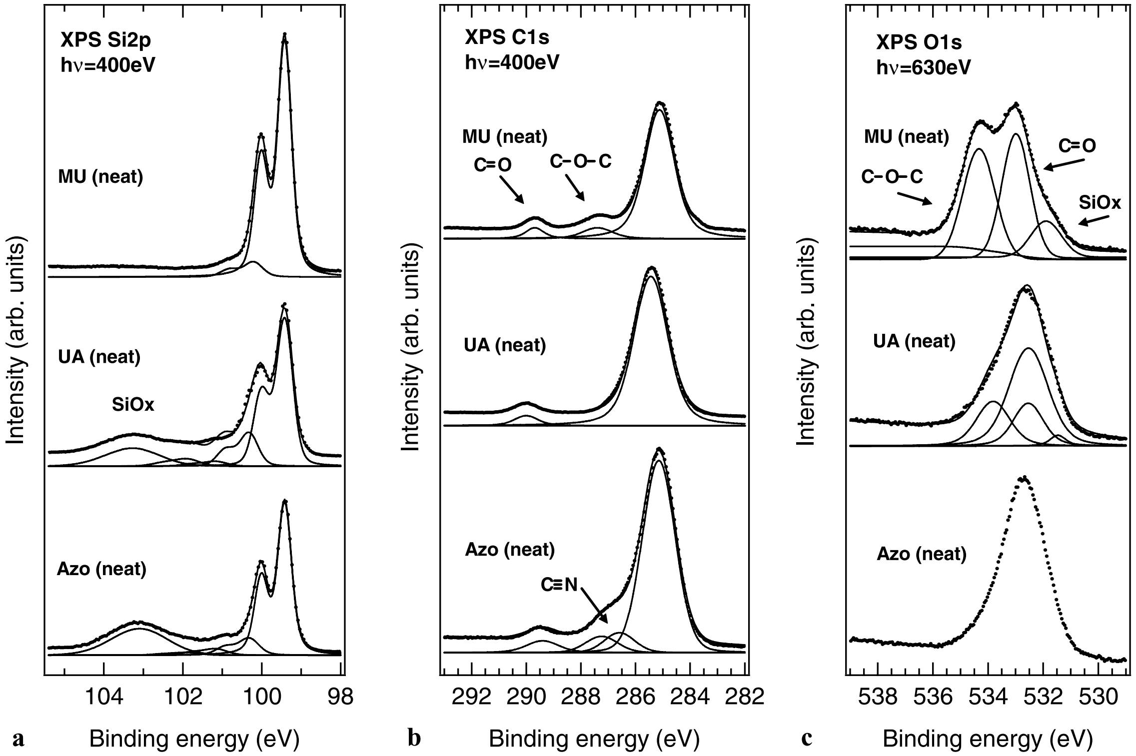

Fig. 2 XP scans of the Si 2p (**a**), C 1s (**b**), and O 1s (**c**) regions of the modified monolayers ($h\nu = 400$ and 630 eV). The sequence starts with **MU**(neat) (*top*), followed by the carboxylic acid **UA**(neat) (*middle*), and the azobenzene SAM **Azo**(neat) (*bottom*)

(5 cm) between the lamp and the lens to cut off the IR irradiation of the lamp. For thermal back relaxations the samples were kept in the dark at room temperature for at least 24 h.

3 Results and discussion

A well established route to build up covalently Si–C linked monolayers on silicon is based on hydrosilylation reactions of ω-unsaturated molecules (e.g., alkenes) with a hydrogen terminated Si surface initiated by light, heat or radicals [32–36]. As illustrated in Fig. 1, ω-functionalized monolayer systems were prepared by hydrosilylation reactions of a freshly prepared Si–H surface with methyl 10-undecenoate (**MU**) for 20 h at 160°C. XPS, FT-IR, and contact angle measurements were used to verify the composition and the quality of the resulting monolayer. The XP survey spectra of a **MU**(neat) SAM shows the presence of carbon, oxygen and the underlying silicon of the substrate, besides a small peak assigned to fluorine originating from the etching step. Figure 2 shows the XP scans of the Si 2p (a), C 1s (b), and O 1s (c) regions of the differently functionalized silicon surfaces. The Si 2p scan of the **MU**(neat) sample (Fig. 2a, top) reveals the typical Si 2p doublet at 99.4 and 100 eV. In addition there is only a small oxygen shifted component at 100.2 eV binding energy which is assigned to Si^{+} [37]. The presence of only the first silicon oxidation state indicates a minor contamination of the silicon surface and thus demonstrates the high quality of the sample. The C 1s region of the same sample exhibits three characteristic peaks at 285.1, 287.4 and 289.7 eV representing the C–C, C–O–C and C=O linked carbons in the **MU**(neat) monolayer (Fig. 2b, top) [13]. In Fig. 2c, the O 1s scan of the same sample exhibits a double peak at 533.0 and at 534.3 eV revealing at least two different oxygen species attributed to the different carboxylic oxygen atoms (C=O and C–O–C) from the monolayer. The small peak at a binding energy of 531.9 eV is attributed to trace levels of oxygen [9, 13].

The grafting solution showed no decomposition of the starting material after 20 h reaction time for hydrosilylation at 160°C as determined by ^{1}H NMR spectroscopy. This is of significance since other ω-functionalized alkenes decomposed during the preparation and gave low quality monolayers with high amounts of oxidized silicon.[2]

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[2] We also investigated Boc- and Dmt-protected dodec-11-enyl amines to prepare amino terminated SAMs but we were not able to obtain high quality monolayers using the same thermal hydrosilylation procedure as described for **MU**. Similar results were reported by Böcking et al. [15]. ^{1}H NMR spectroscopy of the grafting solution after 20 h reaction time at 160°C showed significant amounts of a decomposition product which might be responsible for the oxidation of the silicon substrate.

Table 1 Static water contact angles (°) of the differently modified Si(111) surfaces

Surface	θ
MU(neat)	75.9
UA(neat)	62.8
Azo(neat)	75.4

FT-IR measurements of the pure **MU**(neat) monolayer reveal the significant vibrational modes of the CH$_2$ groups at 2848 and 2917 cm^{-1} as well as the C=O signal at 1744 cm^{-1}, thereby supporting the XPS results. For the modification of the sample with an azobenzene, the carboxylic acid-terminated monolayer was generated by hydrolysis of the methyl ester sample with aqueous HCl at 70°C for 2 h [8]. The Si 2p and C 1s regions of the **UA**(neat) surfaces are illustrated in Fig. 2 (mid panel). The scan of the Si 2p region shows signals at 99.4 and 100.3 eV corresponding to bulk silicon and a new peak around 103.1 eV associated with silicon dioxide, i.e., silicon atoms in the oxidation state +4 (Fig. 2a, middle) [37]. This can be explained by the oxidation of unreacted Si–H sites from the original grafting procedure during the ester hydrolysis in the aqueous media. The strong contribution of the silicon oxide to the O 1s XPS spectrum hampers a reliable analysis of the molecular contribution. From the C 1s scan it becomes obvious that the emission line at 287.4 eV diminishes, and the peaks at 285.4 and 290.0 eV originating from the C–C and C=O carbon atoms slightly shift to higher energy compared to the **MU**(neat) SAMs (Fig. 2b) [9]. Additional contact angle measurements demonstrate a clear change in the wettability behavior of the ester- (75.9°) and the carboxylic acid-terminated monolayers (62.8°), reflecting the increased number of hydrophilic CO$_2$H head-groups (Table 1).

Initial coupling reactions in solution were performed to investigate the covalent binding of azobenzene alcohol **1** to monolayers with free carboxylic acid head-groups, see Fig. 1. Therefore, azobenzene **1** was reacted with 10-undecylenic acid in the presence of HCTU, DMAP, and Hünig's base (DIEA) in acetonitrile. The corresponding 4-[(4-cyanophenyl)diazenyl]benzyl undec-10-enoate (**2**) was isolated in 78% yield after 24 h at rt, work-up and purification.[3] The successful coupling protocol was adapted to the on-chip esterification reaction of the **UA**(neat) surface with alcohol **1** and was monitored by contact angle measurements (Table 1). The reaction was complete within 2 h and the resulting contact angle of 75.4° did not change even after prolonged reaction times (6 h, 18 h).

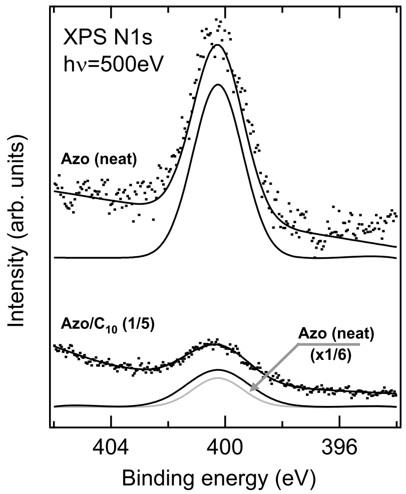

Fig. 3 N 1s region of an **Azo**(neat) and a diluted **Azo**/C$_{10}$(1/5) monolayer. The dashed line corresponds to the sixth part of the **Azo**(neat) signal according to the intended mixing ratio of one to five

The XP spectra of such a modified **Azo**(neat) sample are given in Fig. 2. The Si 2p region reveals no significant changes after the esterification reaction, except for the slightly increased silicon oxide signal at 102.9 eV in comparison to the parent **UA**(neat) surface (Fig. 2a, bottom). The C 1s scan exhibits two main peaks at 285.2 and 289.4 eV corresponding to the carbon atoms of the methylene and the carbonyl groups, respectively, shifted to lower energy in comparison to the carboxylic acid-terminated **UA**(neat) surface. The increased amount of carbon due to the coupling reaction is reflected by the increased intensity of the peak at 285 eV. But the main feature in this spectrum is the shoulder around 287 eV of the broadened signal at 285 eV, which is associated with carbon atoms bound to nitrogen and oxygen atoms. The spectrum is decomposed into two components at binding energies of 286.6 and 287.2 eV attributed to the nitrile (C≡N) and ester (C–O–C) groups, respectively [13, 38]. XPS clearly demonstrates that this contribution is larger than the C–O–C peak in **MU**(neat) even so the O=C peak is smaller. This supports that both nitrile and ester groups are present and suggests the successful transesterification procedure: **MU**(neat)→**UA**(neat)→**Azo**(neat), see Fig. 1. Additional evidence that the attachment of azobenzene **1** to the head groups of the underlying monolayer succeeded is given by the N 1s XP spectra of the **Azo**(neat) sample in Fig. 3. The main peak at 400.3 eV indicates the obvious presence of nitrogen stemming from a SAM with newly formed head groups containing compound **1**.

Furthermore, the covalent linkage of azobenzene **1** and its photochemical activity on the surface was demonstrated by a simple switching experiment monitored by contact angle measurements. The contact angle is known to be very

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[3] Control experiments with a solution of the neat ester **2** in mesitylene (0.2 M) were done in analogy to the other grafting reactions for 20 h at 160°C. This should give a direct comparison between the one-step and the multi-step reaction protocol to prepare monolayers with azobenzene head-groups. Contact angle and XPS measurements showed that the one-step preparation method gave surfaces of less order and quality compared to the on-chip protocols with alcohol **1**. For that reason we focused our investigations on the multi-step on-chip functionalization procedure.

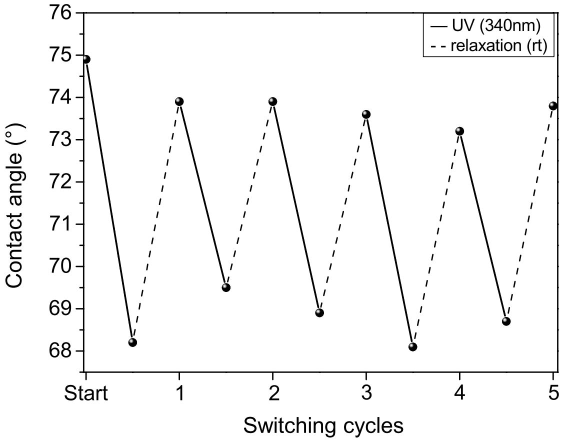

Fig. 4 Repeatable wettability change of an **Azo**(neat) SAM by UV irradiation and thermal relaxation

sensitive to changing variations in the surface composition. Irradiation of an **Azo**(neat) sample with UV light at 340 nm for 10 min caused a decrease of the static water contact angle of 68.2° due to the formation of the *cis* form. It is known that *trans* to *cis* isomerizations of azobenzene molecules are associated with a dramatic change of the dipole moment [22]. Illuminating the azobenzene head-groups of an **Azo**(neat) SAM with UV light generates a more polar surface due to the increased amount of *cis* form. Thus, a better interaction of such a surface with polar liquids results in a better wettability behavior. Similar results were found for azobenzene SAMs on oxidized silicon [23–27]. After 24 h relaxation at room temperature in the dark the contact angle of 73.9° corresponding to the thermodynamically stable *trans* isomer was completely recovered. The switching-relaxation-cycle was repeated 5 times with different samples, as illustrated in Fig. 4. Hence, the preparation of a photo-responsive azobenzene monolayer on Si(111) via a multi-step chemical transformation protocol was demonstrated successfully.

In order to vary the surface density of azobenzene head-groups in the monolayer binary grafting mixtures of 1-decene (**C**$_{10}$) and **MU** with ratios of 5/1 and 10/1 were used. Table 2 illustrates the static water contact angles of these **MU/C**$_{10}$(1/5) and **MU/C**$_{10}$(1/10) SAMs. As expected, the mixed monolayers became more hydrophobic with an increasing amount of the non-polar **C**$_{10}$ component in the grafting mixture. This trend remains after hydrolysis of the ester samples to the carboxylic acid-terminated monolayers, and also for the mixed **Azo/C**$_{10}$ samples.

Table 2 Static water contact angles (°) of differently modified mixed SAMs

Surface	θ	
	1/5	1/10
MU/C$_{10}$	84.2	92.7
UA/C$_{10}$	68.1	75.8
Azo/C$_{10}$	81.0	84.2

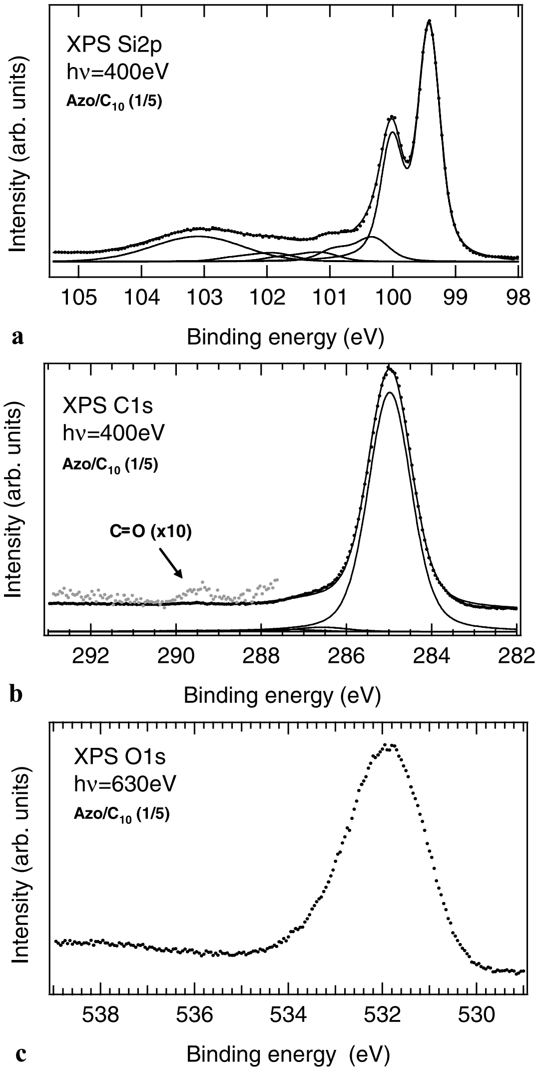

Fig. 5 XP narrow scans of the Si 2p (**a**), C 1s (**b**), and O 1s (**c**) region of an **Azo/C**$_{10}$(1/5) SAM ($h\nu = 400$ and 630 eV). The *dotted line* in (**b**) corresponds to the 10-times magnified C=O signal

Figure 5a illustrates the Si region of a mixed **Azo/C**$_{10}$(1/5) SAM revealing the typical 2p doublet and a SiO_x peak at 102.9 eV which is much smaller than for the **Azo**(neat) sample indicating a better stability and the passivating properties of the mixed SAM, due to the content of non-functionalized decyl chains in the monolayer. The C 1s scan of the **Azo/C**$_{10}$(1/5) monolayer shows the main carbon peak at 284.9 eV and only a small C=O carbon peak at 289.4 eV (Fig. 5b). The oxygen XPS spectrum is again dominated by the silicon oxide component (Fig. 5c).

The N 1s XPS spectrum in Fig. 3 again demonstrates the presence of nitrogen at a binding energy of 400.3 eV. Moreover, the intended dilution was achieved as indicated by the dashed line, which corresponds to the sixth part of **Azo**(neat) sample.

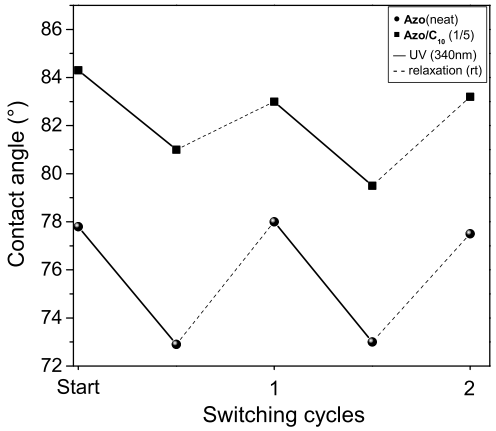

Fig. 6 Contact-angle changes of an **Azo**(neat) [■] and an **Azo/C$_{10}$**(1/5) [●] SAM by UV irradiation/thermal relaxation

Switching experiments were performed to investigate whether the mixed monolayers show changes in the contact angles by UV light illumination or not. Figure 6 illustrates the wettability changes of a mixed **Azo/C$_{10}$**(1/5) and an **Azo**(neat) sample. It is apparent that even the diluted SAMs contain enough azobenzenes to ensure that the UV irradiation causes a significant change of surface properties which can be monitored by wettability measurements.

These results clearly show that the on-chip functionalization of Si(111) via multi-step reactions can be used to incorporate azobenzenes into a preformed underlying alkyl SAM with CO_2Me end-groups. Further experiments will be done to modify the nitrile functionality, e.g., for the attachment of peptide binding sites to test the specificities of the two different isomeric states on the silicon surface. The main advantage of the nitrile group is based on the possible transformation into a CO_2H, CH_2OH, or a CH_2NH_2 moiety after hydrolysis or reduction, respectively, allowing the covalent attachment of many different biomolecules with amino, hydroxy, or acid functionalities.

4 Conclusion

We have synthesized protected methyl ester terminated self-assembled monolayers on Si(111) which were modified on-chip to carboxylic acid-terminated SAMs for the covalent attachment of azobenzene end-groups. The success of our on-chip synthesis is demonstrated by high resolution XPS measurements which allowed us to retrace distinct molecular groups of individual reaction steps. Moreover, mixed monolayers with 1-decene were prepared to vary the surface density of the photochromic units. In addition, the successful switching of azobenzene terminated SAMs was demonstrated by repeatable UV light irradiation-relaxation-cycles.

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