

# Functional monolayers on oxide-free silicon surfaces *via* thiol–ene click chemistry†

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**Thiol–ene click chemistry was used for the attachment of a variety of functional molecules onto oxide-free Si(111) surfaces using very mild conditions; the efficient nature of this coupling strategy allowed for successful light-induced micropatterning and thus provides a novel route towards biofunctional electronics.**

Functional organic monolayers are essential to the development of sensing devices.<sup>1</sup> The precise attachment of functional binding molecules, such as complex sugars<sup>2</sup> and peptides,<sup>3</sup> onto a surface allows for the selective binding and detection of target biomolecules.<sup>4</sup> For electronic applications oxide-free silicon would be the ideal substrate,<sup>5–7</sup> since such surfaces can be easily linked to the infrastructure of semiconductor-based sensing devices. While a lot of work has been done on silicon covered by silicon oxides,<sup>8</sup> such an oxide layer acts as an electrical insulator and the resulting Si–O–Si connected monolayer is prone to hydrolysis. The use of silicon–carbon linkages to attach these functional molecules to oxide-free silicon drastically increases lifetime and robustness of the device.<sup>9,10</sup> However, even the mildest, room-temperature surface modification techniques (visible-light,<sup>11</sup> UV irradiation,<sup>12</sup> and thermal attachment<sup>13,14</sup>) still pose limitations on the range of functional (bio)molecules that can be attached, evidencing the need for a versatile and mild approach towards functional covalent monolayers on silicon.

The great success of click chemistry lies in the mild reaction conditions needed, its high chemoselectivity, and the quantitative yields achieved.<sup>15</sup> Click reactions have also been successfully applied to functionalize inorganic substrates such as gold, glass and silicon.<sup>16–18</sup> Thiol–ene chemistry has recently emerged as an elegant and appealing coupling reaction.<sup>19,20</sup> Very mild reaction conditions, the absence of a metal catalyst, and the ready availability of thiol-functionalized (bio)molecules are distinctive features of this coupling chemistry.

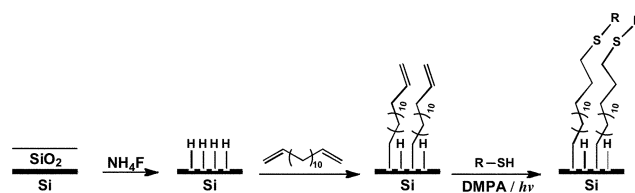
Thiol–ene coupling chemistry has been employed by Bertin and Schlaad as a method to rapidly functionalize glass substrates with polymers.<sup>21</sup> After reaction with (3-mercaptopropyl)trimethoxysilane the resulting thiols were reacted with alkene-functional D-glucose, and the presence of this sugar was demonstrated through binding experiments with fluorescently labeled *Concavilin A*. Buriak and co-workers used thiol–ene

chemistry for the layer-by-layer assembly of dithiols and dienes.<sup>22</sup> This provides an interesting platform for growing covalently bound films of controlled thickness onto oxide-free silicon. Dendrimeric and polymeric approaches have been reported demonstrating both thiol–ene and thiol–yne chemistry. Waldmann and co-workers used polyamidoamine dendrimers attached covalently to silicon oxide surfaces to develop a new method for the site-specific immobilization and patterning of proteins.<sup>23,24</sup> Patton and co-workers used silicon substrates functionalized with silanes to generate a library of highly functional, patterned and multicomponent polymer brush surfaces.<sup>25</sup>

We present here the development of thiol–ene click chemistry as a general, efficient, facile and patternable route to functionalize silicon surfaces under ambient atmosphere without the introduction of silicon oxide that would otherwise be detrimental for electronic performance (Scheme 1).

In order to prepare a Si surface ready for thiol–ene click chemistry, H-terminated Si(111) was reacted with neat 1,13-tetradecadiene (80 °C, argon atmosphere, 16 h†). The presence of a covalently attached organic monolayer was confirmed by the static water contact angle of 96° (corresponding to a C=CH<sub>2</sub>-terminated monolayer), while attenuated total reflection infrared (ATR-IR) spectroscopy demonstrated both the presence of a somewhat disordered alkyl chain (symmetric and antisymmetric CH<sub>2</sub> stretch at 2850 and 2926 cm<sup>-1</sup>, respectively) and of a terminal C=CH<sub>2</sub> moiety (weak signals at 1601 and 3030 cm<sup>-1</sup> from the C=C and C–H stretching mode of C=CH<sub>2</sub>, respectively). The monolayer was further characterized by X-ray photoelectron spectroscopy (XPS). The Si<sub>2p</sub> narrow scan spectrum displays no significant oxide in the 101–104 eV region (Fig. 1). The C<sub>1s</sub> narrow scan shows a single symmetric peak at 285.4 eV, stemming from overlapping signals of C–C and C=C bonds. Moreover, no adventitious fluoride (resulting from etching) was observed in the F<sub>1s</sub> spectra (neither wide nor narrow scan).

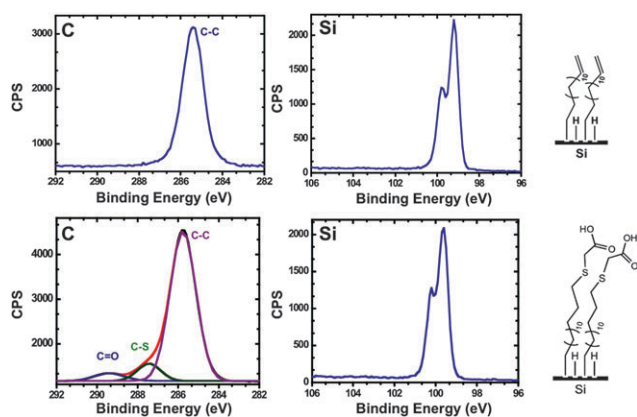
The alkene-terminated monolayers were exposed to 365 nm light in the presence of different thiols and 2,2-dimethoxy-2-phenylacetophenone (DMPA), which acts as a photoinitiator. The coupling reactions were carried out at room temperature



**Scheme 1** Functionalization of silicon surfaces using thiol–ene chemistry.

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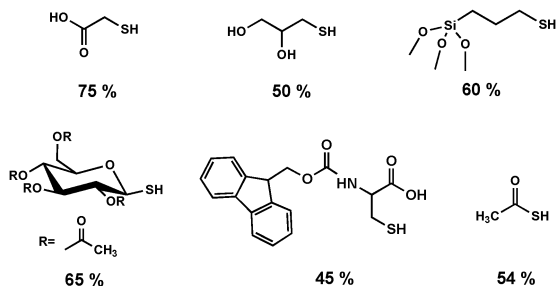


**Fig. 1**  $C_{1s}$  and  $Si_{2p}$  XPS spectra of alkene-terminated monolayer, before (top) and after (bottom) thiol-ene coupling of thioglycolic acid.

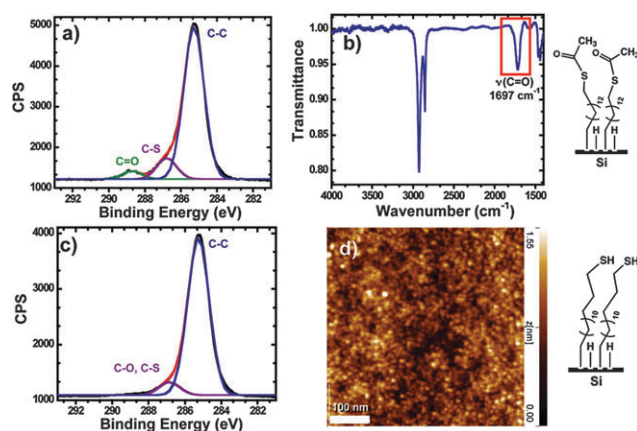
under ambient atmosphere, employing minimal amounts of chlorobenzene or DMF to solubilize the thiols. After thiol-ene click chemistry, the surfaces were washed extensively with chlorobenzene, *n*-hexane and dichloromethane to remove any physisorbed material. First, the coupling of thioglycolic acid to the alkene-terminated monolayer was studied; after 1.5 h of UV exposure a contact angle of  $56^\circ$  was obtained, indicating the formation of a hydrophilic monolayer. Wide-scan XPS data reveal the presence of sulfur, while the  $C_{1s}$  XPS narrow scan reveals the presence of a  $C=O$  bond at 289.4 eV. The  $C_{1s}$  signal can be deconvoluted into three components at 289.4, 287.4 and 285.7 eV that are assigned to  $C=O$ ,  $C-S$  and  $C-C$  carbon atoms, respectively. Based on the area of the  $C=O$  signal at 289.4 eV, a surface coverage of 75% is calculated with respect to the total number of alkyl chains. Importantly, even after thiol-ene functionalization in the presence of oxygen, no trace of surface oxidation is observed.

After the successful attachment of thioglycolic acid, the efficiency and versatility of this approach was investigated for a number of thiols with different functional groups. The alkene-terminated monolayers were exposed to thiolglycerol, 3-mercaptopropyl trimethoxysilane, and the sterically congested thio- $\beta$ -D-glucose tetraacetate and 9-fluorenylmethoxy-carbonyl cysteine (Fig. 2), which in all cases resulted in high surface coverages without  $SiO_2$  formation.

Thiolacetic acid was also employed to functionalize the alkene-terminated monolayers. A water contact angle of  $81^\circ$  was observed for the resulting surface. XPS analysis revealed



**Fig. 2** Thiols employed in surface functionalization, with corresponding surface coverages.



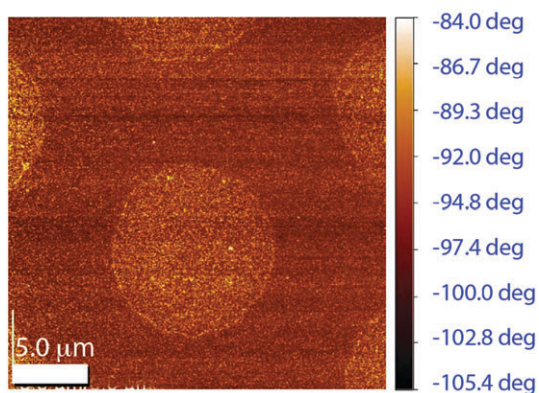
**Fig. 3** (a) XPS  $C_{1s}$  spectrum of thioacetate monolayer; (b) ATR-IR spectrum of thioacetate monolayer; (c) XPS  $C_{1s}$  spectrum of thiol monolayer; and (d) AFM image of thiol monolayer covered with gold nanoparticles, scale bar: 100 nm.

the presence of sulfur, while the narrow scan of the  $C_{1s}$  region indicates the presence of the  $C=O$  bond at 288.7 eV (Fig. 3a). From this signal a surface coverage of 54% is calculated. The thiol-ene coupling was also followed with ATR-IR spectroscopy, which revealed a sharp signal at  $1697\text{ cm}^{-1}$ , corresponding to a thioester group (Fig. 3b). Subsequently, the thioester groups were deprotected with sodium methoxide to expose terminal  $-SH$  moieties. Complete removal of the acetate groups was confirmed by XPS analysis (Fig. 3c). To further evidence the presence of terminal thiols, their interaction with Au nanoparticles was studied by atomic force microscopy (AFM). The thiol-terminated monolayer was immersed in a solution of Au nanoparticles (15 nm) and subsequently rinsed thoroughly. Whereas the thioester monolayer did not display any significant presence of Au nanoparticles, AFM analysis of the thiol-terminated surface revealed a full coverage with these nanoparticles (Fig. 3d).

The attachment of functional (bio)molecules becomes even more appealing with the possibility to pattern distinct areas, to prepare multifunctional structured surfaces.<sup>26</sup> We therefore investigated microcontact printing of thioglycolic acid onto an alkene-terminated monolayer. A PDMS stamp with  $10\ \mu\text{m}$  pillar-like features was covered with the earlier mentioned mixture of thioglycolic acid and DMPA in ethanol, and subsequently brought into contact with the alkene-functional silicon substrate and the surface was irradiated through the stamp for 5 min. After thorough cleaning of the substrate, the surface displays a  $10\ \mu\text{m}$  sphere-pattern in the AFM phase image, confirming successful transfer of the pattern as shown in Fig. 4. Analysis of this surface by XPS again showed no trace of silicon oxide formation. This further demonstrates that thiol-ene chemistry provides an efficient method for metal-free light-induced patterning onto silicon.

We have shown that thiol-ene click chemistry allows for the implementation of functional groups onto oxide-free silicon under very mild conditions. High surface coverages were achieved (45–75%) for a wide variety of functional thiols, while the silicon surfaces did not undergo oxidation.

The ability to attach medium-sized biomolecules bodes well for the functionalization of Si substrates with even larger



**Fig. 4** AFM phase image of the patterned silicon monolayer with thioglycolic acid.

molecules, such as complex sugars, peptides and proteins,<sup>27</sup> while the combination with light-induced patterning adds further potential to this reaction. The approach presented here greatly facilitates the functionalization of oxide-free Si surfaces and hence their application in sensing and optoelectronic devices.

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