Mild methods to assemble and pattern organic monolayers on hydrogen-terminated Si(111)†

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Mild methods to assemble well-ordered organic monolayers of olefins on Si(111) using 2,2,6,6-tetramethyl-1-piperidinyloxy and to pattern these monolayers on the micrometer-size scale using soft lithography are reported.

Combining patterned, organic self-assembled monolayers (SAMs, Fig. 1) with semiconducting surfaces will have a wide impact on the study of biological surfaces and molecular electronics. Although mild methods exist to assemble and pattern SAMs on electrically conducting and insulating substrates such as gold and

Fig. 1 a) A Si(111)-H surface is generated by reacting a clean silicon wafer with 40% NH_4F under N_2. This surface is reacted with different concentrations of TEMPO or derivatives of TEMPO in 1-octadecene to form well-ordered monolayers. b) The different derivatives of TEMPO used to assemble the monolayers.

† Electronic supplementary information (ESI) available: details of method of assembly of SAMs, synthesis of derivatives of TEMPO, and representative examples of XPS spectra. See http://www.rsc.org/suppdata/cc/b5/b503271g/
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glass, methods to assemble SAMs on silicon typically require harsh reagents or conditions.[1–4] Current methods to assemble SAMs on silicon use ultraviolet light, Lewis acids, organic radicals from the decomposition of diacyl peroxides at elevated temperatures, heat, or halogenation of the surface followed by reaction with Grignard reagents.

In this paper we report mild methods to assemble and pattern organic SAMs on hydrogen-terminated Si(111). We assembled SAMs using 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) in the presence of 1-octadecene at room temperature without the need for UV light (Fig. 1).[5] Although TEMPO is a free radical, it is stable at room temperature and unreactive with most functional groups. In addition, we report a mild method to pattern SAMs on Si(111) using soft lithography.

Our method to assemble ordered SAMs has three parts. First, we cleaned silicon wafers in organic solvents, then we removed the native silicon dioxide layer with 5:1 40% NH_4F/48% HF. Next, a thin layer of silicon dioxide was grown by placing the wafer in 1:3 30% H_2O_2/concentrated sulfuric acid at 90 °C for 1 h. Finally, hydrogen-terminated Si(111) was formed using established techniques by immersion of a silicon wafer in 40% NH_4F under an atmosphere of Ar.[6] The silicon shard was placed in a Schlenk flask with TEMPO and 1-octadecene in a glove box under N_2 for 24 h.

We studied the monolayers assembled from 1-octadecene and TEMPO using ellipsometry, contact angle goniometry, and X-ray photoelectron spectroscopy (XPS, Table 1). The ellipsometric data for all of the SAMs were consistent with a monolayer of 1-octadecene rather than a multilayer.

We studied the contact angles of water for monolayers assembled from various concentrations of TEMPO in neat 1-octadecene (entries 1 to 5 in Table 1). The best contact angles of 110° were measured on monolayers assembled from 1.0 and 0.1 mole percent TEMPO. Others have reported that values for the advancing contact angles of water on well-ordered SAMs exposing methyl groups are 110–113°.[1] Values for the advancing contact angles of water on disordered SAMs exposing methylene groups and on polyethylene are 102°.[7] Thus, advancing contact angles of water on an alkyl SAM can provide evidence that the SAM is well-ordered, yet they do not provide definitive proof. Our results indicate that well-ordered monolayers are formed in the presence of TEMPO, but disordered SAMs were obtained from 1-octadecene in the absence of TEMPO (entry 16) and from TEMPO in the absence of 1-octadecene (entry 14).

Interestingly, we saw some oxygen on the surface in the XPS data for monolayers assembled from TEMPO and 1-octadecene (entries 1–5 in Table 1). Oxygen could originate from SiO_2 or from
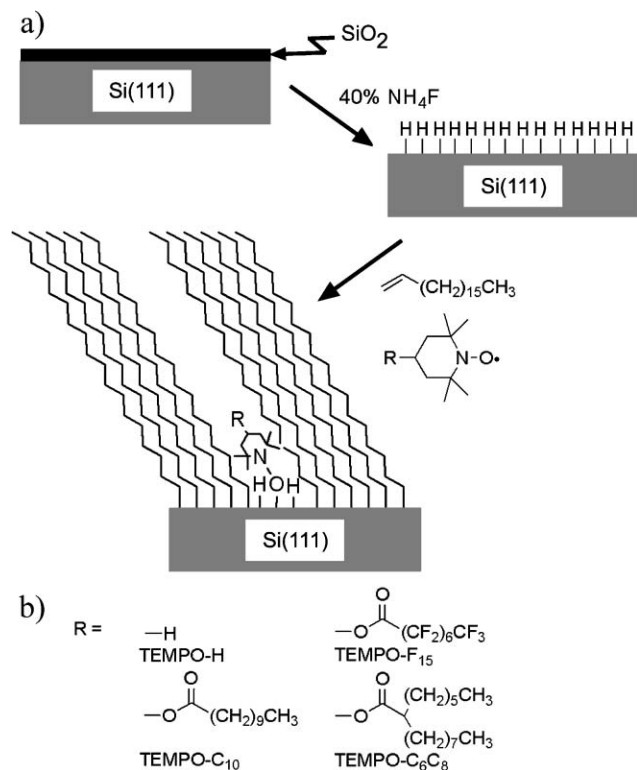
Table 1 The contact angles and atomic compositions from XPS for various monolayers assembled on Si(111)

Entry	[d]Olefin	[a]TEMPO-R (mole%)				[e]d_{ellisp} (Å)	[b]H_2O Contact angle (°)		[c]XPS Atomic composition (%)				
		H	F_{15}	C_{10}	C_6C_8		A	R	SiO_2	Si	F	C	O
1	$C_{18}H_{36}$	10				—	106	104	0	43	0	52	6
2	$C_{18}H_{36}$	1.0				19	110	107	0	39	0	54	7
3	$C_{18}H_{36}$	0.1				21	110	107	0	36	0	59	5
4	$C_{18}H_{36}$	0.01				15	108	107	0	32	0	62	6
5	$C_{18}H_{36}$	0.001				—	106	103	0	34	0	59	7
6	$C_{18}H_{36}$		1			19	114	113	0	31	18	46	4
7	$C_{18}H_{36}$		0.1			17	112	111	0	31	6	58	4
8	$C_{18}H_{36}$		0.01			15	111	110	0	33	2	60	7
9	$C_{18}H_{36}$		0.001			14	110	108	0	35	0	55	10
10	$C_{18}H_{36}$			1.0		17	112	107	0	35	0	60	5
11	$C_{18}H_{36}$			0.1		19	111	105	0	33	0	60	7
12	$C_{18}H_{36}$				1.0	18	111	107	0	34	0	61	6
13	$C_{18}H_{36}$				0.1	20	111	106	0	33	0	61	6
[f]14	None	0.1				—	85	71	5	29	0	18	48
[f]15	None		0.1			—	89	78	2	36	8	24	29
[g]16	$C_{18}H_{36}$					—	102	91	trace	37	0	51	12

[a] These values are the mole percent of TEMPO-R in the 1-octadecene. Values that are blank have a concentration of zero. [b] The errors in the advancing (A) and receding (R) contact angles were approximately $\pm 1°$. [c] We studied the Si(2p), F(1s), C(1s), and O(1s) peaks. The peak corresponding to SiO_2 appeared at approximately 102 eV in the Si(2p) high resolution scan. [d] The olefin was 1-octadecene. [e] The thickness was measured by ellipsometry. The errors in the measurements were ± 5 Å. [f] The TEMPO and TEMPO-F_{15} in these entries were at the same concentrations as TEMPO in entry 3. The monolayers were assembled in hexane. [g] No TEMPO or derivatives of TEMPO were used to assemble this monolayer.

surface-bonded TEMPO. To determine whether TEMPO was bonded to the surface, we assembled monolayers using TEMPO-F_{15} and 1-octadecene. The results in entries 6 to 9 in Table 1 show that the fluorine is present and decreases in concentration as the concentration used to assemble the monolayer decreased. These results demonstrated that TEMPO-F_{15} is indeed bonded to the surface. In summary, some of the oxygen on the surface is due to TEMPO, but due to limitations of XPS, ellipsometry, and structures of the monolayers we can not say whether all of the oxygen on the surface is due to TEMPO.

The presence of TEMPO on the surface raised an interesting problem. TEMPO is expected to increase the disorder in the monolayer of 1-octadecene as it occupies a large cross sectional area near the silicon surface. TEMPO is shorter than 1-octadecene so a gap above TEMPO should exist and disorder adjacent molecules of 1-octadecene. To minimize the disorder caused by TEMPO on the surface, we wished to fill in the "gap" above TEMPO by assembling monolayers from TEMPO-C_{10} and TEMPO-C_6C_8. We expected that monolayers assembled from these derivatives of TEMPO would be more ordered as the C_{10} and C_6C_8 chains would partially fill the gap above TEMPO and increase the order of adjacent 1-octadecene molecules. The results in entries 10 to 13 in Table 1 support this hypothesis as the advancing contact angles increased slightly from 110° for SAMs assembled with TEMPO to 111–112° for SAMs assembled with TEMPO-C_{10} and TEMPO-C_6C_8.

Others have shown that well-ordered monolayers on silicon prevent the oxidation of silicon to silicon dioxide, and disordered monolayers do not prevent this oxidation.[1–4] Thus, the absence of oxidized silicon is further proof that our monolayers are well-ordered. In Table 1 monolayers assembled from 1-octadecene with TEMPO or derivatives of TEMPO showed no evidence of silicon dioxide from the Si(2p) peak in the XPS spectra. In contrast, disordered monolayers from the assembly of TEMPO or

TEMPO-F_{15} in hexane and from neat 1-octadecene without TEMPO had peaks in the XPS spectra that correspond to oxidized silicon (entries 14 to 16 in Table 1).

To further study the quality of the monolayers, we investigated the stability of monolayers from entry 11 in Table 1. Wafers left exposed to ambient atmosphere for 48 days did not exhibit changes in their contact angles and XPS spectra. Thus, the SAMs are stable in air for weeks. We immersed the wafers in $CHCl_3$, toluene, or water for various durations of time. We removed the wafers and characterized them by contact angle goniometry and XPS. If the SAM is well-ordered and stable, we expect that advancing contact angles of water will decrease by less than several degrees and the XPS spectrum will not show the presence of SiO_2.[1] If the SAM is disordered and unstable, the contact angle will significantly decrease and the XPS spectrum will show a peak for SiO_2.[1] The data in Table 2 demonstrate that the SAMs are stable in refluxing $CHCl_3$ (boiling point = 61 °C) for days and in water up to 50 °C. They have limited stabilities in refluxing toluene (boiling point = 111 °C) and refluxing water. These results provide further evidence that we assembled well-ordered monolayers and that they are stable under a range of conditions, thus widening the variety of potential applications.

We developed a method to pattern these monolayers using soft lithography. In our method, PDMS molds were brought into contact with a silicon wafer to form a series of open channels with three sides being PDMS and the fourth side hydrogen-terminated silicon(111) (Fig. 2).

A monolayer terminated with carboxylic acid was assembled in the microfluidic channels. The monolayer only assembled in the channels; whereas, the silicon surface in contact with PDMS was protected from the reagents. After the first monolayer was assembled, we removed the PDMS and assembled a methyl-terminated monolayer on the remainder of the surface. We characterized the patterns using scanning electron microscopy to

Table 2 Stabilities of SAMs (assembled from 0.1 mole % TEMPO-C_{10} and 1-octadecene) immersed in various solvents under ambient pressure

Solvent	Temp.(°C)	Time (h)	[a]Contact angles (°)		[b]XPS Atomic composition (%)			
			A	R	SiO_2	Si	C	O
$CHCl_3$	61	2	110	102	0	31	54	15
		48	110	104	0	30	56	14
		192	106	103	0	30	47	23
Toluene	111	6	109	102	0	32	56	12
		48	104	100	0	29	52	19
		192	102	88	0	30	54	16
Water	[c]20	96	110	104	0	30	58	12
		480	108	103	0	29	59	12
	50	14	111	103	0	30	52	17
		24	110	91	1	30	56	14
[c]$CHCl_3/H_2O$	Reflux	2	109	101	1	27	55	17
		6	110	102	1	26	49	24
		24	91	70	8	21	43	28

[a] We measured the advancing (A) and receding (R) contact angles of water. [b] We studied the Si(2p), F(1s), C(1s), and O(1s) peaks. [c] The wafers were refluxed for 2 h in $CHCl_3$ then refluxed in H_2O for the indicated times.
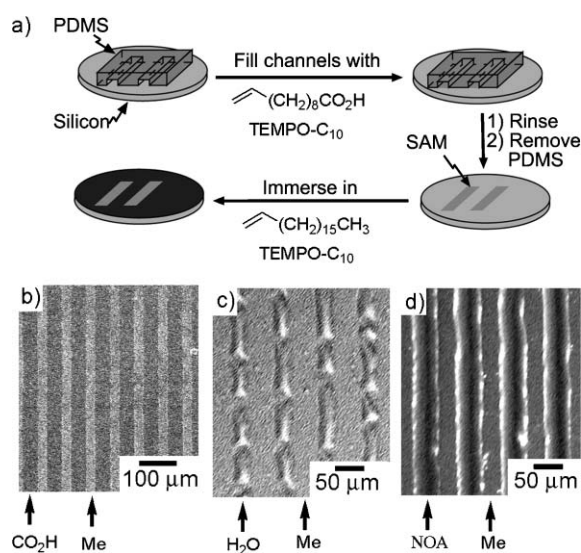

Fig. 2 a) Our method to pattern SAMs on silicon using soft lithography. b) A scanning electron micrograph of a patterned SAM with monolayers terminated with methyl (Me) or carboxylic acid (CO_2H) groups. c) Water condensed on patterned SAMs onto the acid-terminated monolayers. The water drops assume rectangular shapes as they do not wet the methyl-terminated SAMs. d) Lines of NOA-61 were patterned on a silicon wafer by the selective wetting of NOA on acid-terminated SAMs and selective de-wetting on methyl-terminated SAMs.

show the alternating lines of carboxylic acid- and methyl-terminated SAMs (Fig. 2b). In addition, water condensed only on the carboxylic acid-terminated SAMs into rectangular features (Fig. 2c). We also used the difference in wetting between carboxylic acid- and methyl-terminated SAMs to pattern lines of a polymer on the surface. A silicon wafer with a patterned monolayer was immersed in a UV-curable prepolymer (Norland optical adhesive-61) and slowly removed. Upon removal from NOA-61, the prepolymer only coated the acid-terminated SAMs. The prepolymer was cured under UV light and characterized as shown in Fig. 2d.

In conclusion, we report both a mild method to assemble well-ordered SAMs on Si(111) and a mild method for their patterning. These methods enable the assembly and patterning of monolayers directly onto silicon without an intervening layer of silicon dioxide.

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