Fabrication of Ferroelectric Self-assembled Fluorinated Polyether Monolayer on Hydrogen-terminated Si(111) Surface

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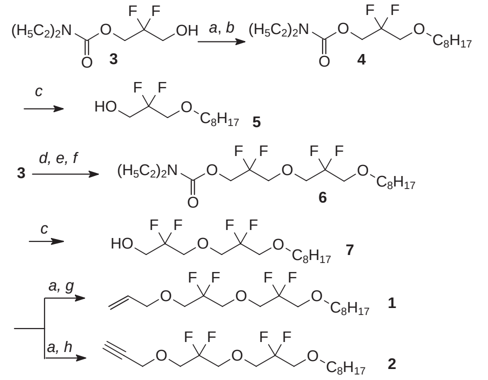
Covalently bonded ferroelectric self-assembled monolayers on silicon surface were fabricated via hydrosilylation of terminally allylated and propargylated fluorine-containing polyether adsorbates on hydrogen-terminated Si(111) substrates. Incomplete polarization—electric field loops indicating ferroelectric property were observed in a range of bias voltage ±300 mV.

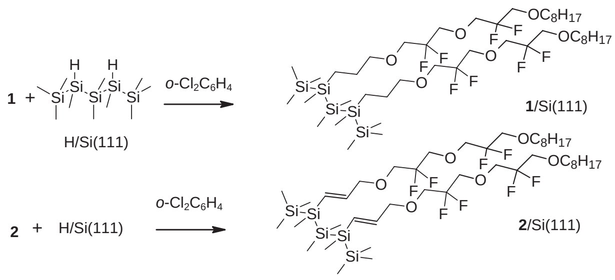
Fabrication of functionalized nanostructure on metallic or inorganic surface is currently receiving a great deal of attention as the "bottom-up" approach of nanotechnology. Particularly, hydrosilylation of terminal alkenes and alkynes onto hydrogen-terminated silicon crystal surfaces, H/Si(111) and H/Si(100), has been recently established to form self-assembled monolayers (SAMs) although only relatively simple unsaturated hydrocarbons were used so far.[1] The use of more sophisticated organic structures is expected to construct functionalized SAMs on the silicon surface for novel electronic devices. Poly(vinylidene fluoride) (PVDF) and its copolymer with trifluoroethene [P(VDF-TrFE)] are diversely applied as ferroelectric or piezoelectric polymers,[2] while relatively high electric voltage alternation is necessary for the polarity switching because the ferroelectricity emerges from rotation of polarized molecules in a highly tangled van der Waals network. Vapor-deposited oligo(vinylidene fluoride) thin film (30–500-nm thick)[3] showed piezoelectric properties although it still needs several tens of volts to switch the molecular orientation. Thin crystalline P(VDF-TrFE) films (2–30 monolayers) by Langmuir–Blodgett (LB) deposition technique showed also ferroelectric properties.[4] Previously, we proposed a more flexible alternative molecular structure unit for dipole alignment: 1,3-dioxy-2,2-difluoropropane, $–OCH_2CF_2CH_2O–$, a potential ferroelectric organic molecular substructure.[5] Immobilization of this organic ferroelectric moiety on silicon surface is expected to form a ferroelectric thin film for the new electronic memory devices. Here, we report preparation of bis(1,3-dioxy-2,2-difluoropropane) ethers and fabrication of functionalized SAM's on Si(111) surface, the first covalently bonded ferroelectric self-assembled monolayer on silicon substrates.

The organic adsorbate molecules for immobilization on silicon surface were designed to include three parts as shown in Scheme 1 (**1** and **2**). One end group has an allyl or propargyl ether structure for the hydrosilylation. The ferroelectric moiety comprises of the two 2,2-difluoropropane-1,3-dioxy units. The last part is an octyl group for the hydrophobic self-assembly. Preparation of polyethers **1** and **2** was started from the previously reported singly protected 2,2-difluoro-1,3-propanediol **3**,[5] which was first alkylated with iodooctane and NaH to give urethane **4** (75%). Deprotection of **4** with $LiAlH_4$ afforded alcohol **5** (76%).



(a) NaH/DMF; (b) $C_8H_{17}I$; (c) $LiAlH_4$/THF reflux; (d) 2,6-lutidine/CH_2Cl_2, −10 °C; (e) Tf_2O; (f) NaH/**5**/THF; (g) $CH_2{=}CHCH_2Br$; (h) $HC{\equiv}CCH_2Br$.

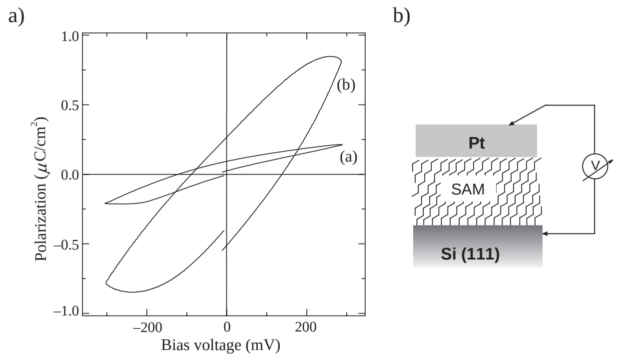
Scheme 1. Preparation of fluorinated polyether adsorbate molecules **1** and **2**.



Scheme 2. Hydrosilylation of **1** and **2** on H/Si(111).

Since elongation of a ferroelectric polyether unit under the usual Williamson conditions using *p*-toluenesulfonate of **3** was unsuccessful because of the unusually low reactivities of the fluorinated tosylate and sodium alkoxide of **3**, it was achieved by the reaction with an excess amount of trifluoromethanesulfonate of alcohol **3**, which was prepared from **3** and trifric anhydride in the presence of 2,6-lutidine, to give polyether–urethane **6** (93%). Deprotection of **6** gave alcohol **7** by treatment with $LiAlH_4$ (90%). Finally, alcohol **7** was allylated or propargylated with allyl bromide or propargyl bromide in the presence of NaH to afford **1** and **2** in somewhat low yields, 28 and 35%, respectively.

Hydrogen-terminated silicon substrate, H/Si(111), was prepared from boron-doped silicon wafer [Si(111)] (ca. 10 × ca. 10 × 0.42 mm; resistivity $\rho = 14.4 \pm 0.4\,\Omega\cdot\text{cm}$) according to the method reported by Buriak et al.[6] SAM formation on H/Si(111) surface was carried out by immersing the hydrogenated silicon substrate into 1.0 mM solution of polyether **1** or **2**



(a) **1**/Si(111) (b) **2**/Si(111)

Figure 1. a) Bias voltage–polarization profile of SAMs on Si(111) surface at room temperature: (a) **1**/Si(111), (b) **2**/Si(111). Averages of three scans were taken. b) Schematic representation of ferroelectric characteristics measurements using a ferroelectric test system (FCE-1, TOYO Corporation).

in *o*-dichlorobenzene at room temperature for 10 h (Scheme 2). In the previous works,[1,7] thermal or photolytic activation was employed for the homolytic cleavage of Si–H bonds. However, these activations are not necessary unless a radical incompatible solvent such as toluene or mesitylene is used. After successive washing of the silicon substrate with *o*-dichlorobenzene, acetone, methanol, and water under sonication and drying under vacuum, ellipsometric analysis indicated that nanometer-thick membranes were formed on the silicon surface [**1**/Si(111): $d = 16.2 \pm 0.5$ Å, **2**/Si(111): $d = 15.6 \pm 0.3$ Å].[8]

Ferroelectric characterization of **1**/Si(111) and **2**/Si(111) at room temperature was carried out by polarization–bias voltage hysteresis measurement between the range of the −300–+300-mV bias voltage scans (100 Hz) using a thin film capacitor as schematically illustrated in Figure 1b. The samples were prepared by sputtering platinum metal on the SAM surface for an upper microelectrode (diameter: 0.2 mm) and an edge of the substrate was shaved for the counter electrode to consist the thin film capacitor. As shown in Figure 1a, incomplete polarization–bias voltage hysteresis loops of ferroelectric materials were observed in the both SAM substrates of non-short-circuited samples. Usually, the hysteresis curve of the ferroelectric materials forms a closed symmetric sigmoid loop because of the delayed movement of dipoles as shown by the multilayer LB membrane of ferroelectric P(VDF-TrFE).[4a] Since larger bias voltage (>±500 mV) caused conduction due to a tunneling current, and saturated polarizations of the SAMs were not obtained, the loops were incomplete. The unsymmetrical feature of polarization hysteresis of **1**/Si(111) is quite similar to the polarization hysteresis loop of a two-monolayer LB membrane of P(VDF-TrFE).[4a] From the longitudinal scale of the polarization–voltage hysteresis loops at 0-V bias, the residual polarization of **2**/Si(111) [Figure 1a(b)] appears approximately three times more than that of **1**/Si(111) [Figure 1a(a)]. While the absolute scale of polarization in Figure 1a is not rigorous owing to lack of saturated polarizations and the inter-electrode distances which determine the precise electric field range, difference between the apparent residual polarizations of the SAMs may suggest that the acetylenic **2** gives more densely packed SAM than **1**.

The ferroelectric properties of these SAM materials are derived from aligned dipole moments perpendicular to the molecular axis induced by molecular rotation of the fluorinated polyether moiety in response to scanning of the poling bias voltage as similar as fluorinated ferroelectric polymers.[9] The speculated molecular lengths of the linear *trans*-zigzag conformers are ca. 25 Å for **1** and **2** according to a molecular modeling study (molecular mechanics).[10] The observed SAM thicknesses (15–16 Å) were slightly smaller than the estimated value of the film thickness (20 Å) with ca. 36° tinting of the molecular axis from the normal to the Si(111) face. Usually, stable ground-state conformation of ethers is a mixture of trans and gauche conformers.[11] Particularly, the stable conformation of ethers with electron-withdrawing groups such as a difluoromethylene group is likely to be gauche due to the anomeric effect.[12] Molecular modeling study[13] suggested that there exist many energetically comparable twisted conformers of the fluorinated polyethers in the ground state and the average length of the SAM molecules are expected to be shorter than the dipole-aligned *trans*-zigzag conformer under the electric field poling conditions. In order to examine the effects of molecular length of the adsobates and the number of ferroelectric molecular units, investigation to prepare the adsorbate molecules with more ferroelectric units is now in progress.

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