Exploration of the chemical bonding forms of alkoxy-type organic monolayers directly attached to silicon

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Alkoxy-type organic monolayers on hydrogen-terminated silicon were prepared from 1-undecanol (UN), 1-nonanol (NO), 1-heptanol (HP), and 4-phenylphenenol (PP). These monolayers were characterized based on x-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR). XPS spectra showed that the lowest amount of SiO_x oxide on the sample of the UN monolayer. On the other hand, a SiO_x peak was clearly observed for the HP, NO, and PP monolayers. The generation of SiO_x in the PP monolayer may have been due to steric hindrance of the aromatic rings. The $-CH_2-$ region in the FT-IR spectra showed that shorter alkyl chains promoted the formation of gauche conformers in the monolayer. This increase of gauche conformers was determined to have caused the generation of SiO_x in the alkyl monolayers. © *2004 American Vacuum Society.* [DOI: 10.1116/1.1759353]

Self-assembled monolayers (SAMs) formed through the chemical reaction between 1-alkene and hydrogen-terminated silicon (Si–H)[1–6] are an attractive material to employ for molecular electronic devices, since such a monolayer is directly attached to Si without the need for an oxide interlayer. This is a clear advantage for electronic applications of the SAMs and distinguishes them from organosilane SAMs on Si. Furthermore, such a directly bonded SAM is chemically more durable to HF solution more than an organosilane SAM.[7]

The formation of organic monolayers using alcohol has also attracted much research attention. This is an attractive route since many organic compounds are available as precursors, offering an advantage for material fabrications. Organic monolayers formed in this fashion provide us with many options to fabricate materials. However, there have been few reports on the formation of organic monolayers via Si–OR bonds (alkoxy-type monolayers) on hydrogen-terminated silicon.[8,9] Furthermore, evidence of such monolayer formation has not yet been presented. In this study, we both present evidence demonstrating the formation of alkoxy-type monolayers and characterize them.

We formed SAMs on Si–H from various precursor organic molecules including 1-undecanol (UN), 1-dodecanol, 1-heptanol (HP), and 4-phenylphenol (PP). Angle-resolved x-ray photoelectron spectroscopy (AR-XPS) and Fourier transform infrared spectroscopy (FT-IR) were used to characterize the obtained monolayers.

Si (111) sample substrates (*p* type) were treated by an ultraviolet-ozone cleaning method until their surfaces became completely hydrophilic with a water contact angle of almost 0°. The substrates were cleaned ultrasonically in acetone, methanol, and de-ionized water in that order. The substrates were further etched in aqueous HF solution (5 vol %) at room temperature for 5 min in order to remove surface oxide and to terminate their surface with hydrogen. UN, 1-nonanol (NO), 1 HP and PP (Tokyo Kasei Co Ltd.) were used as received. The purity of all chemicals is 99.0%. The hydrogen-terminated Si(111) (i.e., Si–H) substrates were alkoxylated as follows. Each hydrogen-terminated silicon substrate was immersed with a precursor in a flask with a reflux condenser. Nitrogen gas was continuously supplied to the reaction system in order to prevent oxygen from being mixed. After N_2 purge for 3 h, the flask was heated. The detail experimental conditions are listed in Table I. After the alkoxylation, the samples were ultrasonically cleaned in toluene, methanol, and de-ionized water in order to remove physical adsorbates.

The samples were characterized by XPS (AXIS, Shimadzu-Kartos), attenuated total reflection spectroscopy (DIGILAB, FTS7000), ellipsometer (Philips, PZ2000), and water contact angle analyzer (KRUSS, DSA10 Mk2). XPS measurements were performed under the following condi-

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TABLE I. Preparation conditions for the organic monolayers.

	Reaction temperature (°C)	Reaction time (h)
1-Undecanol	150	5.0
1-Nodecanol	120	5.0
1-Heptanol	120	5.0
4-Phenylphenol	100	5.0

TABLE II. Water contact angle and film thickness of UN, NO, HP, and PP monolayers.

Monolayer	Water contact angle (deg)	Film thickness (nm)	
		Measured	MO predicted
UN	110	1.3	1.5
NO	110	1.1	1.2
HP	110	0.9	1.0
PP	80	1.0	1.0

tions. The monochromatic x-ray source was operated at 10 mA and 12 kV. The pass energy was 10 eV and the electron take-off angles were 90°, 60°, and 30°. All binding energies were referenced to $Si\,2p$ (*n*-type Si) at 99.3 eV. The water contact angle and film thickness of the monolayers are listed in Table II. The monolayers with CH_3 termination, i.e., the UN, NO, and HP monolayers, all had a water contact angle of 110°. This water contact angle is ideal for a CH_3-terminated organic monolayer. On the other hand, the water contact angle of the PP monolayer was 80°, which is close to that of a phenylsilane self-assembled monolayer. The measured film thicknesses of the UN, NO, HP, and PP monolayers were 1.3, 1.1, 0.9, and 1.0 nm, respectively. In order to validate our film thickness measurements, we predicted the molecular length by semiempirical molecular orbital (MO) calculations with the AM1 Hamiltonian. Our MO calculations, also listed in Table II, show that the molecular lengths of the UN, NO, HP, and PP molecules were 1.5, 1.2, 1.0, and 0.9 nm, respectively. The calculated values were generally larger than our measured ones, however the amount of difference is very reasonable since the molecular chains have some tilt angles.

Figure 1 shows XPS Si_{2p} and C_{1s} spectra of the alkoxylated silicon sample surfaces at takeoff angles of 90°, 60°, and 30°. No SiO_2 peaks were observed in the Si_{2p} spectra of the UN monolayer at any of the takeoff angles. The main peak seen in all of the Si_{2p} spectra originated from $Si_{2p1/2}$ and $Si_{2p3/2}$. In addition, other peaks probably exist on the shoulder of the $Si_{2p1/2}$ peak. This indicates that Si–H bonds might have been replaced by those of Si–OR. Separation

with two Gaussian distribution functions showed the presence of Si–OR. For all takeoff angles of the C_{1s} spectra, only a peak originating from hydrocarbon ($-CH_2-$) was detected. This indicates that the preparation process did not cause any impairment of the alkyl chains. The film thickness of the monolayer as roughly estimated by attenuation of the Si_{2p} spectra, was found to be ~1.4 nm.[10,11] This is consistent with the film thickness acquired by ellipsometry. Thus, these results verify that the prepared organic layer is indeed a monolayer. On the other hand, SiO_x peaks were observed in the Si_{2p} spectra of the NO, HP, and PP monolayers. These may be due to shorter alkyl chains and/or steric hindrance of the aromatic structure. The shorter alkyl chains may have caused the generation of gauche conformers in the monolayer.[12] This would result in the low packing density in the monolayer. Steric hindrance of the aromatic structure would also have caused the same effect.

Figure 2 shows FT-IR spectra of the organic monolayers. These were differential spectra, in which the spectrum of the hydrogen-terminated silicon was subtracted from that of the organic monolayer. These peaks were observed from 2800 to 3000 cm^{-1} for the UN, NO, and HP monolayers; the $-CH_2-$ symmetric stretching mode (~ 2854 cm^{-1}, ν_1), the $-CH_2-$ asymmetric stretching mode (~ 2924 cm^{-1}, ν_2), and the $-CH_3$ asymmetric stretching mode (~ 2962 cm^{-1}, ν_3). The ν_1 and ν_2 mode peaks increased with a decrease in the length
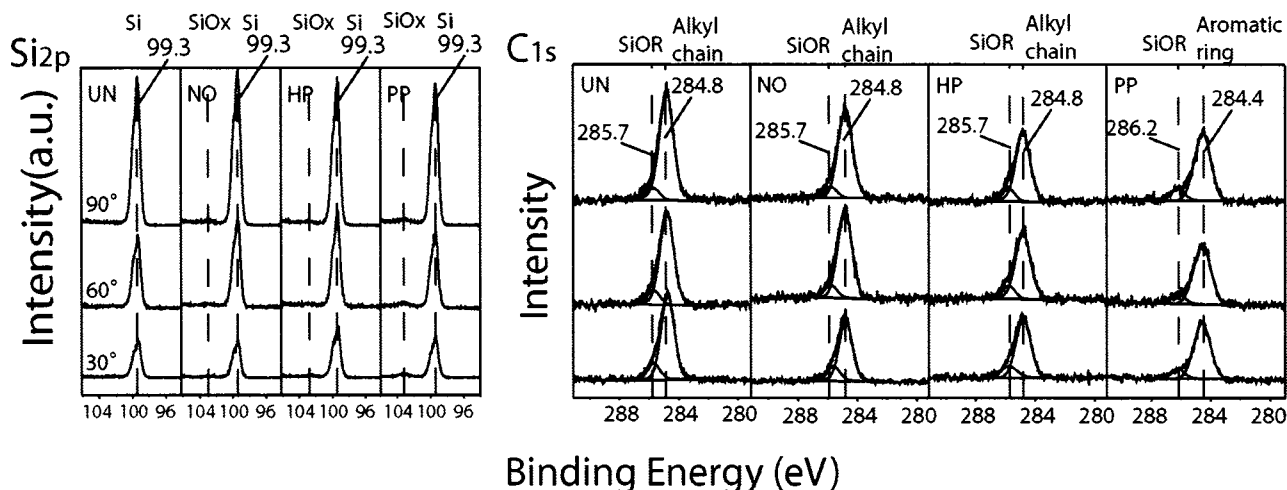

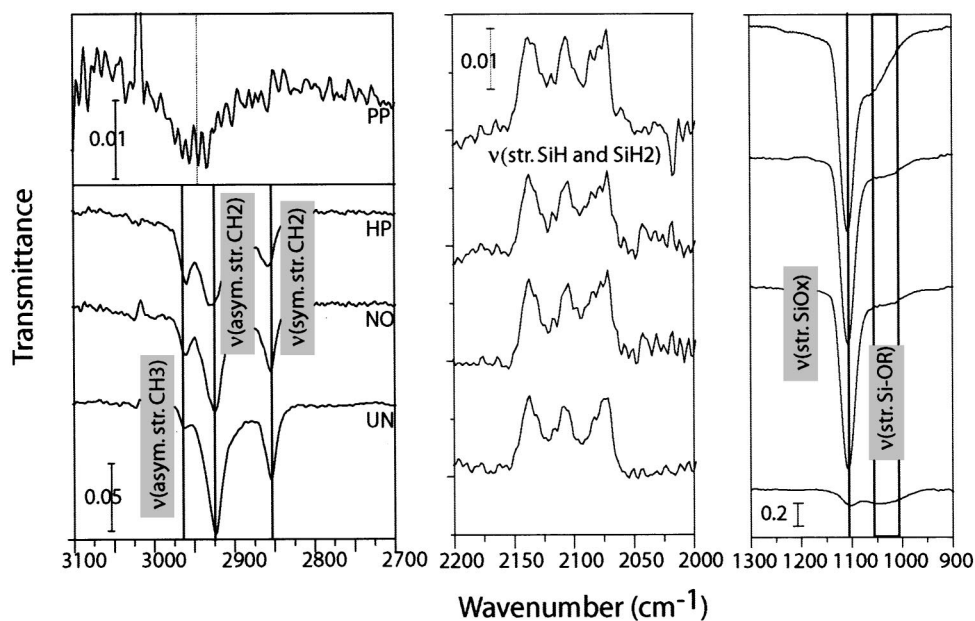FIG. 1. AR-XPS spectra of UN, NO, HP, and PP monolayers on silicon substrates.

FIG. 2. FT-IR spectra of UN, NO, HP, and PP monolayers on silicon substrates.

of the alkyl chain. On the other hand, the ν_3 mode peak decreased with a decrease in the length of the alkyl chain, as shown in Fig. 2. These results indicate that gauche conformers were generated with decreased chain length. For the PP monolayer, the CH stretching mode was observed at ~ 2900 cm^{-1}. A strong and a weak peak were observed from 1000 to 1100 cm^{-1}. Generally, the strong peak would have originated from silicon oxide such as SiO$_x$. The weak peak originated from Si–OR. This weak peak was assigned to the symmetric stretching mode originating from Si–OR bonds. Furthermore, the intensity of the Si–H stretching mode (~ 2100 cm^{-1}) after the preparation became weak compared with that of hydrogen-terminated silicon. These results provide evidence that the organic molecules were attached to the silicon by Si–OR bonds, which formed at the interface between the silicon and the organic monolayers see Table III.

Generally NH$_4$F enchant produces atomically flat surface on silicon (111) substrate. The surface termination is mainly Si–H bonds. On the other hand, HF enchant produces the termination of SiH, SiH$_2$, and SiH$_3$. We could obtain important information about the reaction mechanism of organic monolayers formation by comparing those on these different surfaces.

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TABLE III. Vibrational modes of methylene and methyl groups in UN, NO, and HP monolayers.

Monolayer	$-CH_2-$ symmetric	$-CH_2-$ asymmetric	$-CH_3-$ asymmetric
UN	2854	2924	2962
NO	2854	2923	2960
HP	2857	2926	2959